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GLASS MANUFACTURE

WALTER RUSSELL BASSETT

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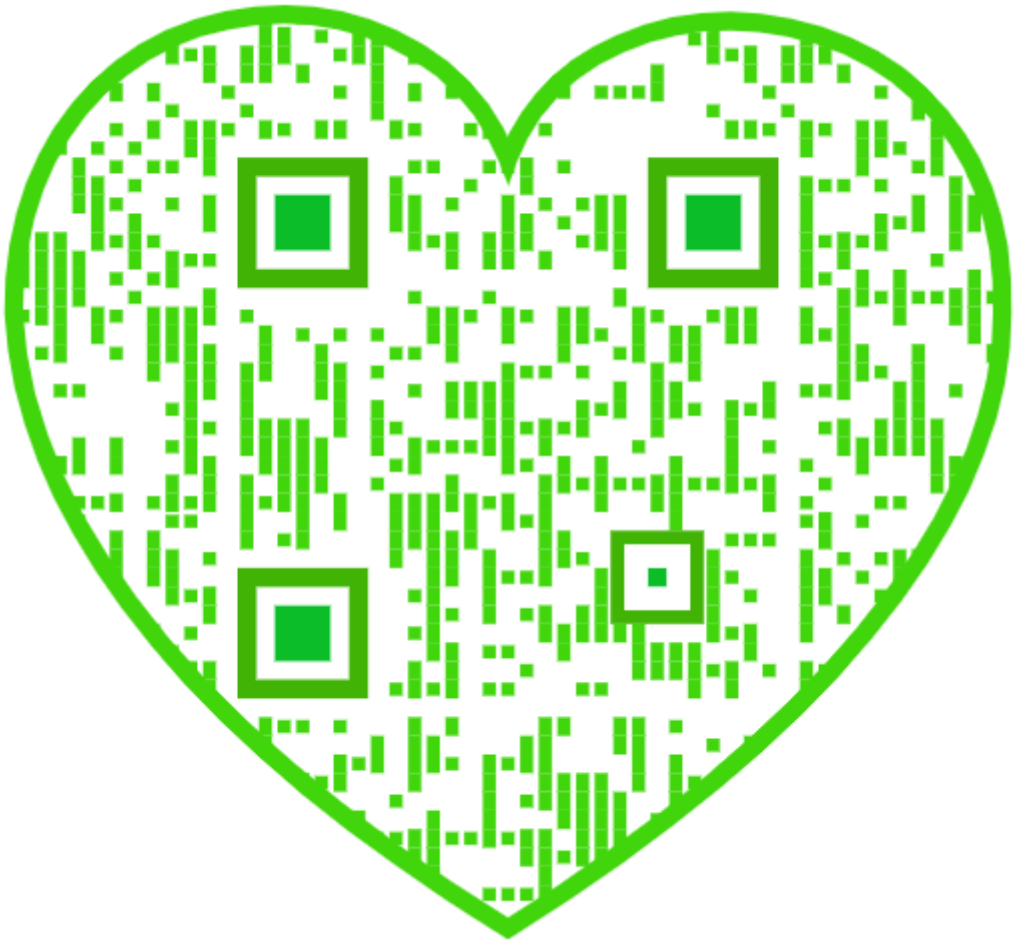

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GLASS MANUFACTURE

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GLASS MANUFACTURE

BY

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PREFACE TO THE FIRST EDITION

THE present volume on Glass Manufacture has been written chiefly for the benefit of those who are users of glass, and therefore, makes no claim to be an adequate guide or help to those engaged in glass manufacture itself. For this reason the account of manufacturing processes has been kept as non-technical as possible; no detailed drawings of plant or appliances have been given, and only a few illustrative diagrams have been introduced for the purpose of avoiding lengthy verbal descriptions. In describing each process the object in view has been to give an insight into the rationale of each step, so far as it is known or understood, and thus to indicate the possibilities and limitations of the process and of its resulting products rather than to provide a detailed guide to the technique of the various operations. The practical aim of the book has further been safeguarded by the fact that the processes described in these pages are, with the exception of those described as obsolete to the author's definite knowledge, in commercial use at the present time. For this reason many apparently ingenious and beautiful processes described in earlier books on glass have not been mentioned here, since the author could find no trace of their employment beyond the records of the various patents involved. On the other hand the reader must be warned to bear in mind that the peculiar conditions of the glass manufacturing industry have led to the practice on the part of manufacturers of keeping their processes as secret as possible, so that the task of the author who would give an accurate account of the best modern processes used in any given department of the industry is beset with great difficulties. The author has endeavoured

to steer the best course open to him under these circumstances, and he would appeal to the paucity of glass literature in the English language as evidence of the difficulty to which he refers.

In addition to these difficulties, which arise largely from considerations of a commercial nature, the writer of a book on glass is further confronted with technical difficulties of no inconsiderable order. As already indicated, the aim of the present author has been to describe processes from the point of view of principles and methods rather than as mere rule-of-thumb descriptions of manufacturing manipulations, but in doing this he is met at every turn by the fact that from the scientific side the greater part of the field of glass manufacture is a "terra incognita." In making this statement the labours of many eminent scientific workers are by no means forgotten, but the entire field is so large and beset with such great experimental difficulties that even the labours of a list of investigators that includes the names of Fraunhofer and Faraday, Stokes, Hopkinson, Abbé and Schott, have resulted in little more than an accumulation of empirical data which, while they have been productive of great direct practical results, have left the science of glass still in a very elementary condition. To take two examples in illustration of this fact we may mention the question of the connection between chemical composition and any of the physical properties of glass, such as refraction and dispersion of light, and on the more mechanical side the question why all processes, such as rolling or moulding, which involve the contact of hot glass with metal result in a roughening of the glass surface. The former question has been studied by several of the investigators named above, Schott and Abbé having particularly devoted an enormous amount of labour and money to the study of the question, with results which have proved disappointing from the scientific point of view. By prolonged experimenting and the employment of a costly system of trial and error an important series of novel and useful glasses has been produced by these workers, but no law by whose aid the optical properties of a glass of given chemical composition could be predicted has yet been discovered, and as a summary

of the known facts only the vaguest general principles are available for the guidance of those who wish to produce glasses of definite properties. The same applies in a similar degree to most of the other properties of glass, with the exception, perhaps, of density and thermal expansion ; attempts to generalise from the known data of a limited number of glasses generally meet with unqualified failure. The conclusion which one is forced to admit is that the fundamental principles underlying the nature and constitution of glasses have yet to be discovered. A study of the other question mentioned above as an example of the limitations of our knowledge leads to the same conclusion ; an almost endless succession of inventors have busied themselves with devices for overcoming the roughening action of rollers and moulds upon glass, but without any real success. A long list of other examples of the same kind could be given, our knowledge of the physical and chemical principles underlying many of the phenomena met with in glass manufacture being deplorably deficient. It will thus be seen that to write a truly scientific account of glass manufacture is at the present time impossible, and the reader is asked to bear this in mind if he should find the chemical or physical explanations given in this book less frequent or less adequate than could be desired.

Having dwelt somewhat emphatically on the limitations of our present scientific knowledge as applied to glass manufacture, it is perhaps scarcely necessary at the present time to emphasise the fact that this state of affairs should act as the strongest incentive to further investigation of the whole subject. The difficulty, however, lies in the fact that such investigation can scarcely be carried on by voluntary workers in ordinary laboratories, but must be undertaken with the active help of glass manufacturers at their works. Glass is essentially a substance that cannot be satisfactorily handled in small quantities, particularly so far as all the phenomena connected with its production and manipulation while hot are concerned ; the influences of containing vessels, of furnace gases and of rapid cooling are all enormously exaggerated if ounces instead of hundredweights

or tons of glass are used for experimental purposes, and these influences and others of the same nature vitally affect all the results of small-scale laboratory operations. The progress of our scientific knowledge of glass—and the consequent development of the glass industry from its present state where rule-of-thumb and "practical experience" still hold excessive sway—lies in the hands of those concerned in the industry itself. It must be admitted that to undertake such work involves the expenditure of much time and money on the part of a manufacturer, while the field is so large and the problems so complicated that any adequate return cannot be promised for the *immediate* future; on the other hand the very size of the field and the difficulty of the problems offers the promise of the greatest ultimate reward; a really important scientific discovery in connection with glass would be certain to bring in its train industrial developments whose limits it is impossible to foresee. The industrial success of the glass-works of Schott in Jena is often quoted as a brilliant example of commercial success resulting from purely scientific investigations in this actual field; an example of still greater magnitude is furnished by the success of the aniline dye works of Germany, which are built up on purely scientific achievements. The glass industry as a whole, supplying some of the absolute necessaries of modern life, should be capable of offering the greatest rewards to success, and the example of other industries has shown that *ultimate* success is bound to reward properly-conducted and perseverant scientific research. Nowhere is this more urgently needed than in the whole field of glass manufacture.

The author is indebted to Mr. W. C. Hancock for valuable assistance in the reading of proofs and various suggestions in connection with the contents of this book.

PREFACE TO THE SECOND EDITION

In the eleven years which have elapsed since the first edition of this book was written, the Glass Industry has undergone very great development; so far as the British industry is concerned, most of this development has—under the stimulus of war—been crowded into the period of the four years 1915 to 1919 inclusive, and much of this represents a supreme effort made under adverse conditions, an effort of which the glass manufacturers of Great Britain have good reason to be proud. In endeavouring to revise the present work in such a manner as to bring it into reasonable conformity with the present position of the industry while not too greatly exceeding the original framework, it has not been possible to deal with the history and development of each process. All that has been attempted is to introduce brief accounts of modern developments—of which the automatic blowing-machine of the Owens type may be taken as an example—and to modify expressions of views and anticipations where these have not been borne out by the course of events.

Perhaps the most important modification introduced into the book is the chapter (Chapter IV.) dealing with *Refractories*. This subject has assumed a position of such fundamental importance in relation to glass manufacture that treatment in considerably greater detail appeared to be justified.

Some typical analyses of various kinds of glassware are given in an Appendix; the author has preferred to group them together in this

manner, which affords ready comparison, rather than to scatter them through the various chapters.

The author wishes to express his indebtedness to two of his colleagues at the National Physical Laboratory—Mr. W. H. Withey and Mr. E. A. Coad-Pryor—for valuable help in the preparation of this edition, the former in regard to the chemical testing and analysis of glass and the latter in connection with refractories.

TEDDINGTON,
December 18th, 1918.

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GLASS MANUFACTURE

CHAPTER I

THE PHYSICAL AND CHEMICAL PROPERTIES OF GLASS

ALTHOUGH the term "glass" denotes a group of bodies which possess in common a number of well-defined and characteristic properties, it is difficult to frame a satisfactory definition of the term itself. Thus while the property of transparency is at once suggested by the word "glass," there are a number of true glasses which are not transparent, and some of which are not even translucent. Hardness and brittleness also are properties more or less characteristic of glasses, yet very wide differences are to be found in this respect also, and bodies, both harder and more fragile than glass, are to be found among minerals and metals. Perhaps the only really universal property of glasses is that of possessing an amorphous structure, so that vitreous bodies as a whole may be regarded as typical of "structureless" solids. All bodies, whether liquid or solid, must possess an ultimate structure, be it atomic, molecular or electronic in character, but the structure here referred to is not that of individual molecules but rather the manner of grouping or aggregation of molecules.

In the great majority of mineral or inorganic bodies the molecules in the solid phase are arranged in a definite grouping and the body is said to have a crystalline structure; evidences of this structure are generally visible to the unaided eye or can be revealed by the microscope. Vitreous bodies on the other hand are characterised

by the entire absence of such a structure, and the mechanical, optical and chemical behaviour of such bodies is consistent only with the assumption that their molecules possess the same arrangement, or rather lack of arrangement, that is found in liquids.

The intimate resemblance between vitreous bodies and true liquids is further emphasised when it is realised that true liquids can in many instances pass into the vitreous state without undergoing any critical change or exhibiting any discontinuity of behaviour such as occurs during the freezing of a crystalline body. In the latter class of substances the passage from the liquid to the crystalline state takes place at one definite temperature, and the change is accompanied by a considerable evolution of heat, so that the cooling of the mass is temporarily arrested. In the case of glasses, on the other hand, the passage from the liquid to the apparently solid condition is gradual and perfectly continuous, no evolution of heat or retardation of cooling being observed even by the aid of the most delicate instruments. We are thus justified in speaking of glasses as " congealed liquids " ; the process of congealing in this case involves no change of structure, no re-arrangement of the molecules, but simply implies a gradual stiffening of the liquid until the viscosity becomes so great that the body behaves like a solid. It is, however, just this power of becoming exceedingly stiff or viscous when cooled down to ordinary temperatures that renders the existence of vitreous bodies possible. All glasses are capable of undergoing the change to the crystalline state when kept for a sufficient time at a suitable temperature. The process which then takes place is known as " devitrification," and sometimes gives rise to serious manufacturing difficulties.

Molten glass may be regarded as a mutual solution of a number of chemical substances—usually silicates and borates. When cooled in the ordinary way these bodies remain mutually dissolved, and ordinary glass is thus simply a congealed solution. The dissolved substances have, however, natural freezing-points of their own, and if the molten mass be kept for any length of time at a temperature

a little below one of these freezing-points, that particular substance will begin to solidify separately in the form of crystals. The facility with which this will occur depends upon the properties of the ingredients and upon the proportions in which they are present in the glass. In some cases this devitrification sets in so readily that it can scarcely be prevented at all, while in other cases the glass must be maintained at the proper temperature for hours before crystallisation can be induced to set in. In either of these cases, provided that the glass is cooled sufficiently rapidly to prevent crystallisation, the sequence of events during the subsequent cooling of the mass is this: as the temperature falls further and further below the natural freezing-point of one or other of the dissolved bodies, the tendency of that body to crystallise out at first rapidly increases; as the temperature falls, however, the resistance which the liquid presents to the motion of the molecules increases at a still greater rate, so that two opposing forces are at work, one of them an increasing tendency towards crystallisation, the other a still more rapidly increasing resistance to any change. There is thus for every glass a certain critical range of temperature during which the greatest tendency exists for the crystallising forces to overcome the internal resistance; through this range the glass must be cooled at a relatively rapid rate if devitrification is to be avoided; at lower temperatures the crystallising forces require increasingly longer periods of time to produce any sensible effect, until, as the ordinary temperature is approached, the forces of internal resistance entirely prevent all tendency to crystallisation.

The phenomena just described in reality constitute the natural limit to the range of bodies which can be obtained in the vitreous state: as we approach this limit the glass requires more and more rapid cooling through the critical range of temperature, and is thus more and more liable to devitrify during the manufacturing processes, until finally the limit is set when no industrially feasible rapidity of cooling suffices to retain the mass in the vitreous state.

While the range of bodies that can be obtained in the vitreous

state is very large, only a comparatively small number of substances are ordinarily incorporated in industrial glasses. With the exception of certain special glasses used for scientific purposes, such as the construction of optical lenses, thermometers and vessels intended to resist unusual treatment, all industrial glasses are of the nature of mixed silicates of a few bases, viz., the alkalies, sodium and potassium, the alkaline earths, calcium, magnesium, strontium, and barium, the oxides of iron and aluminium (generally present in minor quantities), zinc oxide, and lead oxide. The manner in which these various elements enter into combination and solution with one another has been much investigated, and the more general conclusions have been anticipated in what has been said above. It is abundantly evident that glasses are not definite chemical compounds, but rather solutions, in varying proportions, of a series of definite compounds in one another. In many cases the actual constitution of industrial glasses is so complex as, for the present at all events, to baffle adequate chemical expression.

One of the factors that limit the range of possible compositions of glasses has already been indicated, and two others must now be discussed. For industrial purposes, the cost and rarity of the ingredients becomes a vital bar at a certain stage; thus the use of such elements as lithium, thallium, etc., is prohibitively costly. In another direction the glass-maker is very effectively restrained by the limitations of his furnaces as regards temperature. The presence of excessive proportions of silica, lime, alumina, etc., tends to raise the temperature required for the free fusion of the glass, and when this temperature seriously exceeds 1600° C., the manufacture of the glass in ordinary furnaces becomes impossible. Thus pure silica can be converted into a glass possessing very valuable properties, but the requisite temperature cannot be attained in regenerative gas-fired furnaces such as are ordinarily used by glass manufacturers. This limitation has, however, been overcome to a considerable extent in the manufacture of pure silica glass, sometimes known as vitreous silica. The high temperatures required in this

case are obtained—on a relatively small scale, it is true—by means of electric or oxy-acetylene furnaces. None the less, vitreous silica has become an important commercial product, whether in the translucent and relatively cheap form produced by the fusion of sand in an electric furnace, or in the more perfect variety obtainable in smaller sizes either in the form of articles for laboratory use or even in small blocks suitable for the production of small lenses. The limitation of temperature, therefore, can no longer be regarded as insuperable, but the special methods required when the range of 1600° C. is exceeded involve special prices for the objects produced as compared with more ordinary varieties of glass.

A further limitation in the choice of chemical components is placed upon the manufacturer by the actual chemical behaviour of the glass both during manufacture and in use. As regards chemical behaviour during manufacture, it must be borne in mind that, although glasses are of the nature of solutions rather than of compounds, yet these solutions tend towards a state of saturation; thus a glass rich in silica and deficient in bases will readily dissolve any basic materials with which it may come in contact, while, on the other hand, a glass rich in bases and poor in acid constituents such as silica, boric acid or alumina, will readily absorb acid bodies from its surroundings. During the process of melting, glass is universally contained in fireclay vessels. These are chosen, as regards their own chemical composition, so as to offer to the molten glass as few as possible of those materials in which the glass itself is deficient; yet a limit arises in this respect also, since glasses very rich in bases, such as the very dense lead and barium glass made for optical purposes, rapidly attack any fire-clay with which they may come in contact. The finished glass also betrays its chemical composition by its chemical behaviour towards the atmospheric agents, such as moisture and carbonic acid, with which it comes in contact; glasses containing an excessive proportion of alkali, for example, are found to be seriously hygroscopic and to undergo rapid decomposition, especially in a damp atmosphere.

Within the limits set by these considerations, the glass manufacturer chooses the chemical composition of his glass according to the purpose for which it is intended; for most industrial products the cheapest and most accessible raw materials that will yield a glass of the requisite appearance are employed, while for special purposes the dependence of physical properties upon chemical composition is utilised, as far as possible, in order to attain a glass specially suited to the particular requirements in question. Thus the flint and barium glasses used for table and ornamental ware derive from the dense and strongly refracting oxides of lead and barium their properties of brilliancy and weight. The fusibility and softness imparted to the glass by the presence of these bases further adapts it to its purpose by facilitating the complicated manipulations to which the glass must be subjected in the manufacturing processes.

Taking our next example at almost the opposite extreme, the hardest "combustion tubing," which is intended to resist a red heat without appreciable softening, is manufactured by reducing the basic contents of the glass to the lowest possible degree, especially minimising the alkali content, and using the most refractory bases available, such as lime, magnesia, and alumina in the highest possible proportions. Such glass is, of course, difficult to melt, and special furnaces are required for its production, but on the other hand this material meets requirements which ordinary soda-lime or flint glass tubing could never approach. Another instance of these refractory glasses is to be found in the Jena special thermometer glasses and in the French (Tonnelot) "Verre dur"; the best of these glasses show little or no plasticity at temperatures approaching 500° C., and have thus rendered possible a considerable extension of the range of the mercury thermometer. Further modification of chemical composition has resulted in the production of glasses which are far less subject to those gradual changes which occur in ordinary glass when used for the manufacture of thermometers—changes which vitiated the accuracy of most early

thermometers. A still more extensive adaptation of chemical composition to the attainment of desired physical properties has been reached primarily as a result of the labours of Schott and Abbé, in the case of optical glasses. The work of these men, and the developments which have followed from it, both at the works founded by them at Jena and elsewhere, have so profoundly modified our knowledge of the range of possibilities embraced by the class of vitreous bodies, that it is not at all easy at the present time to realise the former narrow and restricted meaning of the term "glass." The subject of the dependence of the optical properties of glass upon chemical composition will be referred to in detail in Chapter XII. on "Optical Glass," but the outline of the influence of composition on properties here given could not be closed without some reference to this pioneer work.

The chemical behaviour of glass surfaces, to which we have already referred, is of the utmost importance to all users of glass. The relatively neutral chemical behaviour of glass is, in fact, one of its most useful properties, and, next to its transparency, most frequently the governing factor in its employment for various purposes. Thus the entire use of glass for table-ware depends primarily upon the fact that it does not appreciably affect the composition and flavour of edible solids or liquids with which it is brought into contact—a property which is only very partially shared even by the noble metals. Again, the use of glass windows in places exposed to the weather would not be feasible if window-glass were appreciably attacked by the action of water or of the gases of the atmosphere. For these general purposes, it is true, most ordinary glasses are adequately resistant, but this degree of perfection in this respect is only the outcome of the centuries of experience which the practical glass-maker has behind him in the manufacture and behaviour of such glass. When, however, a higher degree of chemical resistance is required for special purposes, as for instance when glass is called upon to resist exposure to hot, damp climates, or is intended to contain corrosive liquids,

the rules which are an adequate guide to the glass-maker in meeting ordinary requirements are no longer sufficient, particularly when the glass is expected to meet other stringent requirements as well. It has, in fact, frequently happened that a glass-maker, in striving to improve the colour or quality of his glass, as regards freedom from defects, brilliancy of surface, etc., has spoilt the chemical durability of his products. The reason lies in the fact, long known in general terms, that an increased alkali content reduces the chemical resistance of glass, while at the same time such an increase of alkali is the readiest means whereby the glass-maker can improve his glass in other respects by making it more fusible and easier to work in every way.

This subject of the chemical stability of glass surfaces attracted much attention during the later part of last century, and careful investigations on the subject were carried out, particularly at the Reichsanstalt (Imperial Physical Laboratory) at Charlottenburg. More recently (since 1914) this subject has also received much attention in England, where researches have been carried out, notably by Sir Herbert Jackson at King's College, London, and at the National Physical Laboratory. As a result glasses of British manufacture are now available which answer the most stringent requirements. Similar efforts have also been made, with successful results, in France and America.

Leaving aside the inferior glasses, containing, generally, more than 15 per cent. of alkali, the behaviour of glass surfaces to the principal chemical agents may be summed up in the following statements. Pure water attacks all glass to a greater or lesser extent; in the best glasses the prolonged action of cold water merely extracts a minute trace of alkalies, but in less perfect kinds the extraction of alkali is considerable on prolonged exposure even in the cold, and becomes rapidly more serious if the temperature is raised. Superheated water, *i.e.*, water under steam pressure, becomes an active corroding agent, and the best glasses can only resist its action for a limited time. For the gauge-glass tubes of

steam boilers working at the high pressures which are customary at the present time, specially durable glasses are required and can be obtained, although many of the gauge-tubes ordinarily sold are quite unfit for the purpose, both from the present point of view and from that of strength and "thermal endurance."

In certain classes of glass, the action of water, especially when hot, is not entirely confined to the surface, some water penetrating into the mass of the glass to an appreciable depth. The exact mechanism of this action is not known, but the writer inclines to the view that it arises from a partial hydration of some of the silica or silicates present in the glass. If such glasses be dried in the ordinary way and subsequently heated, the surface will be riddled with minute cracks, some glass may even flake off, and the whole surface will be dulled. As such penetrating action sometimes takes place—in the poorer kinds of glass—by the action of atmospheric moisture when the glass is merely stored in a damp place, it is often mistaken for "devitrification." This latter action, however, is not known to occur at the ordinary temperature, although glass when heated in a flame frequently shows the phenomenon; it is, however, entirely distinct from the surface "corrosion" just described.

Water containing alkaline substances in solution acts upon all glasses in a relatively rapid manner; it acts by first abstracting silica from the glass, the alkali and lime being dissolved or mechanically removed at a later stage. Water containing acid bodies in solution—*i.e.*, dilute acid—on the other hand acts upon most varieties of glass decidedly less energetically than pure water, and much less vigorously than alkaline solutions; this peculiar behaviour probably depends upon the tendency of acids to prevent the hydration of silica, this substance being thereby enabled to act as a barrier to the solvent action of the water upon the alkaline constituents of the glass. The better varieties of glass are also practically impervious to the action of strong acids, although certain of these, such as phosphoric and hydrofluoric, exert a rapid action on all kinds of glass. Only certain special glasses, containing

an excessive proportion of basic constituents and of such substances as boric or phosphoric acid, are capable of being completely decomposed by the action of strong acids, such as hydrochloric or nitric, the bases entering into combination with the acids, while the silicic and other acids are liberated.

In connection with the action of acids upon glass, mention should be made of certain special actions that are of practical importance. The dissolving action of hydrofluoric acid upon glass is, of course, well known. This acid is used in practice both in the liquid and gaseous form, and also in that of compounds from which it is readily liberated (such as ammonium or sodium fluoride), for the purpose of "etching" glass, and also in decomposing glass for purposes of chemical analysis. Next in importance ranks the action of carbonic acid gas upon glass, especially in the presence of moisture. The action in question is probably indirect in character; the moisture of the air, condensing upon the surface of the glass, first exerts its dissolving action, and thus draws from the glass a certain quantity of alkali, which almost certainly at first goes into solution as alkali hydrate (potassium or sodium hydroxide); this alkaline solution, however, rapidly absorbs carbonic acid from the air, and the carbonate of the alkali is formed. If the glass dries, this carbonate forms a coating of minute crystals on the surface of the glass, giving it a dull, dimmed appearance; this, however, only occurs ordinarily with soda glasses, since the carbonate of potassium is too hygroscopic to remain in the dry solid state in any ordinary atmosphere. Potash glasses are, as such, no more stable chemically than soda glasses, but they are for the reason just given less liable to exhibit a dim surface. If the dimming process, in the case of a soda glass, has not gone too far, the brightness of the surface of the glass may be practically restored by washing it with water, in which the minute crystals of carbonate of soda readily dissolve, while separated silica is removed mechanically. An attempt made to clean the same dimmed surface by dry wiping would only result in finally ruining the surface, since the small sharp crystals of

carbonate of soda would be rubbed about over the surface, scratching it in all directions.

The dimming process in the case of the less resistant glasses is not only confined to the formation of alkaline carbonates; the films of alkaline solution which are formed on the surface of glass form a ready breeding-ground for certain forms of bacteria and fungi, whose growth occurs partly at the expense of the glass itself; the precise nature of these actions has not been fully studied, but there can be little doubt that silicate minerals—and glass is to be reckoned among these—are subject to bacterial decomposition, a well-known example in another direction being the "maturing" of clays by storage in the dark, the change in the clay being accompanied by an evolution of ammonia gas. In the case of glass it has been shown that specks of organic dust falling upon a surface may give rise to local decomposition. In this connection it is interesting to note the effect of the presence of a small proportion of boric acid in some glasses. The presence of this ingredient in small proportions is known to render the glass more resistant to atmospheric agencies, and more especially to render it less sensitive to the effects of organic dust particles lying upon the surface. It has been suggested—probably rightly—that the boric acid, entering into solution in the film of surface moisture, exerts its well-known antiseptic properties, thus protecting the glass from bacterial and fungoid activity.

The durability of glass under the action of atmospheric agents is a matter of such importance that numerous efforts have been made to establish a satisfactory test whereby this property of a given glass may be ascertained without awaiting the results of experience obtained by actual use under unfavourable conditions. One of the earliest of the tests proposed consisted in exposing surfaces of the glass to the vapour of hydrochloric acid. For this purpose some strong hydrochloric acid is placed in a glass or porcelain basin, and strips of the glass to be tested are placed across the top of the basin, the whole being covered with a bell-jar. After

several days the glass is examined, and as a rule the less stable glasses show a dull, dimmed surface as compared with the more stable ones. A more elaborate form of test depends upon the fact that aqueous ether solutions react readily with the less stable kinds of glass; if a suitable dye, such as iod-eosin, be dissolved in the water-ether solution, then the effect upon the less stable glasses when immersed in the solution is the formation of a strongly adherent pink film. The density or depth of colour of this film may be regarded as measuring the stability of the glass; the best kinds of glass remain practically free from coloured film. In its application to optical glass the test is made on a freshly fractured surface which, after careful brushing with a clean, dry brush, is first exposed to a moist atmosphere for a week in a closed vessel. The glass is then dipped in an aqueous ether solution of iod-eosin (terta-iodo-fluorescein) where the pink film is formed; it is then washed by dipping in ether, which removes the excess of iod-eosin. The pink film is then dissolved off in water and the colour of the resulting solution is matched against a standard solution containing a known amount of sodium-iod-eosin. In this way a quantitative estimation of the amount of alkali liberated from the glass surface is obtained. Optical glasses have been classified in five categories according to the results given under this test, as follows:—

Class "H_1"	gives 0 to 5	milligrammes	of iod-eosin	per sq.	metre.
Class "H_2"	,, 5 to 10	,,	,,	,,	,,
Class "H_3"	,, 10 to 20	,,	,,	,,	,,
Class "H_4"	,, 20 to 40	,,	,,	,,	,,
Class "H_5"	,, 40 to 80	,,	,,	,,	,,

In its application to glass-ware for use in chemical laboratories the test is used in a slightly different form. The vessels are first given a preliminary cleaning by standing with water at 20° C. for one week. They are then emptied and refilled with fresh water and allowed to stand for another week, again at 20° C. A measured volume of this water, now containing the alkalies dissolved from the glass, is then taken and shaken with a measured volume of the

ether solution of iod-eosin. The water then becomes coloured by the formation of sodium iod-eosin and some free iod-eosin is also dissolved in it. The latter is removed by shaking with ether saturated with water. The colour of the remaining water solution is then estimated by comparison with a standard solution as before.

There is no doubt that this test, if the working conditions are very carefully observed, gives a sharp classification of glasses, but there is good reason to doubt whether this classification agrees with their true durability in practice, since certain glasses which have proved very satisfactory in this respect in practical use all over the world were classed among the less stable kinds by this test. On the other hand certain dense lead and barium glasses which are not very stable in practice, yet receive a high classification under the iod-eosin test, as this only takes note of *alkali* liberated.

Recently a method of testing glass for durability has been developed in which the glass is exposed to superheated water in an autoclave under a steam pressure of 4 to 5 atmospheres. At the correspondingly high temperature, water attacks glass with comparative rapidity, and the test is based on the assumption that the resisting power of glass against the action of water in the autoclave is proportional to its power of resistance under more ordinary conditions. This assumption has yet to be finally established, but the test furnishes a means of quantitative comparison between different kinds of glass which—in its present form—is only applicable to hollow-ware such as laboratory vessels. It might, however, be applied to optical and other glass if its trustworthiness is demonstrated. The extent to which the glass has been attacked is measured both by determining the alkali content of the water which has stood in the vessel during the test and also by evaporating this solution and weighing the total solid residue, and this residue will include, besides the alkali, any silica, lead, barium, etc., which may have been extracted from the glass by the superheated water.

Before leaving the subject of the chemical behaviour of glass, a reference should be made to the changes which glass undergoes

when acted upon by light and other radiations. Under the influence of prolonged exposure to strong light, particularly to sunlight, and still more so to ultra-violet light, or the light of the sun at high altitudes, practically all kinds of glass undergo changes which generally take the form of changes of colour. Glasses containing manganese especially are apt to assume a purple or brown tinge under such circumstances, although the powerful action of radium radiations is capable of producing similar discoloration in glasses free from manganese. Apart from these latter effects, of which very little is known as yet, there can be no doubt that the action of light brings about chemical changes within the glass, but it is by no means easy to ascertain the true nature of these changes, although they most probably consist in a transfer of oxygen from one to another of the oxides present in the glass. Although it has not been definitely proved, it seems very unlikely that the glass either loses or gains in any constituent during these changes. Good examples of the changes undergone by glass under the action of sunlight are frequently found in skylights, where the oldest panes sometimes show a decided purple tint which they did not possess when first put in place. The glass spheres of the instruments used for obtaining records of the duration of sunshine at meteorological stations also show signs of the changes due to light—the glass of these spheres when new has a light greenish tint, but after prolonged use the colour changes to a decided yellow. The coloured glass in stained-glass windows also shows signs of having undergone changes of tint in consequence of prolonged exposure to light ; glass removed from ancient windows usually shows a deeper tint in those portions which have been protected from the direct action of light by the leading in which the glass was set, and it is at least an open question whether the beauty of ancient glass may not be, in part, due to the mellowing effect of light upon some of the tints of the design. This photo-sensitiveness of glass is also of some importance in connection with the manufacture of photographic plates. It has been found that if the glass plate of a strongly-developed negative be cleaned,

a decided trace of the former image is retained by the glass, and this image is apt to reappear as a "ghost" if the same glass is again coated with sensitive emulsion and again exposed and developed. The best makers of plates recognise this fact and do not re-coat glass that has once been used for the production of a negative.

CHAPTER II

THE PHYSICAL PROPERTIES OF GLASS

The Mechanical Properties of Glass are of considerable importance in many directions. Although glass is rarely used in such a manner that it is directly called upon to sustain serious mechanical stresses, the ordinary uses of glass in the glazing of large windows and skylights depend upon the strength of the material to a very considerable extent. Thus in the handling of plate-glass in the largest sheets, the mechanical strength of the plates must be relied upon to a considerable extent, and it is this factor which really limits the size of plate that can be safely handled and installed. The same limitation applies to sheet-glass also, for, although its lighter weight renders it less liable to break under its own weight, its thinner section renders it much more liable to accidental fracture. In special cases, also, the mechanical strength of glass must be relied upon to a considerable extent. Gauge tubes of high-pressure boilers, port-hole glasses in ships, the glass prisms inserted in pavement lights, and the glass bricks which have found some use in France, as well as champagne bottles and mineral water bottles and syphons, are all examples of uses in which glass is exposed to direct stresses. It is, therefore, a little surprising that while the mechanical properties of metals, timbers, and all manner of other materials have been studied in the fullest possible manner, those of glass have received very little attention, at all events so far as published data go. One reason for this state of affairs is probably to be found in the fact that it is by no means easy to determine the strength of so brittle and hard a body as glass. As a consequence even the scanty data available can only be regarded as first approxi-

mations. The following data are only intended to give an idea of the general order of strength to be looked for in glass:—

Tensile strength:

From 1 to 4 tons per sq. in. (Trautwine).
„ $\frac{1}{3}$ to $1\frac{1}{4}$ „ „ „ (Henrivaux).
„ 2 to $5\frac{1}{2}$ „ „ „ (Winkelmann and Schott).
„ 5 to 6 „ „ „ (Kowalski).

Crushing strength:

From 9 to 16 tons per sq. in. (Trautwine).
„ 3 to 8 „ „ „ (Winkelmann and Schott).
„ 20 to 27 „ „ „ (Kowalski).

Of the above figures the experiments of Winkelmann and Schott are probably by far the most reliable, but these refer to a series of special Jena glasses, selected with a view to determining the influence of chemical composition on mechanical properties, and, unfortunately, this series does not include glasses at all closely resembling those ordinarily used for practical purposes. The attempt to connect tensile and crushing strength with chemical composition was also only very partially successful; but the results serve to show that the chemical composition has a profound influence on the mechanical strength of glass, so that by systematic research it would probably be possible to produce glasses of considerably greater mechanical strength than those at present known. It must be noted in this connection that the mechanical properties of glass depend to a very considerable extent upon the rate of cooling which the specimen in question has undergone. It is well known that by rapid cooling, or quenching, the hardness of glass can be considerably increased; such treatment also increases the strength both as against tension and compression, and numerous processes have been put forward for the purpose of utilising these effects in practice. Unfortunately the "hardened" glass thus obtained is extremely sensitive to minute scratches, and flies to pieces as soon as the surface is broken, when the great internal

stress which always exists in such glass is thereby relieved. All these peculiarities are, of course, dependent as to their degree upon the rapidity with which the glass has been cooled, and the aim of inventors in this field has been to devise a rapid cooling process which should strike the happy mean between the increased strength and the induced brittleness resulting from quenching. Thus processes for "tempering" glass by cooling it in a blast of steam or in a bath of hot oil or grease have been brought forward; but, although some such glass is manufactured, no very extensive practical application has resulted.

Elasticity and Ductility of Glass.—In a series of glasses investigated by Winkelmann and Schott, the modulus of elasticity (Young's Modulus) varied from 3,500 to 5,100 tons per sq. in., the value being largely dependent upon the chemical composition of the glass. Measurable ductility has not been observed in glass under ordinary conditions except in the case of champagne bottles under test by internal hydraulic pressure; in these tests it was found that a permanent increase of volume of a few tenths of a cubic centimetre could be obtained by the application of an internal pressure just short of that required to burst the bottle—pressure of the order of 18 to 30 atmospheres being involved. This small permanent set has been ascribed to incipient fissuring of the glass, and this explanation is probably correct. On the other hand, glass is capable of decided flow under the *prolonged* action of relatively small forces; the behaviour of large discs of worked optical glass suggests some such action, but a more familiar and well-marked example is found in the behaviour of ordinary glass tubing. If this is stored in a slightly inclined position—as in leaning against the wall in a corner—it gradually sags to a very marked extent, so that glass tubing which is required to remain straight must be kept lying flat on a shelf. In this respect glass behaves in a manner which recalls the behaviour of pitch or of sealing-wax, and like these materials it is essentially a liquid of very high viscosity.

Hardness is a property of some importance in most of the applica-

tions of glass. The durability of glass objects which are exposed to handling or to periodical cleaning must largely depend upon the power of the glass to resist scratching; this applies to such objects as plate-glass windows and mirrors, spectacle and other lenses, and in a minor degree to table-ware. On the other hand, the exact definition and means of measuring hardness are not yet satisfactorily settled. Experimenters have found it very difficult to measure the direct resistance to scratching, since it is found, for example, that two glasses of very different hardness are yet capable of decidedly scratching each other under suitable conditions. Resort has therefore been had to other methods of measuring hardness; the method which, from the experimental point of view, is, perhaps, the most satisfactory, depends upon principles laid down by Hertz and elaborated experimentally by Auerbach. This depends upon measuring the size of the circular area of contact produced when a spherical lens is pressed against a flat plate of the same glass with a known pressure. Auerbach himself found some difficulty in deciding the exact connection between the "indentation modulus" thus determined and the actual hardness of the glass. This method is, therefore, of theoretical interest rather than of use in testing glasses for hardness. A test of a more practical kind consists in exposing specimens of the glasses to be tested to abrasion against a revolving disc of cast-iron fed with emery or other abrasive, and to measure the loss of weight which results from a given amount of abrading action under a known contact pressure. If a number of specimens of different glasses are exposed to this test at one time, a very good comparison of their power of resisting abrasion can be obtained. It is not quite certain that this test measures the actual "hardness" of the glass, but it affords some information as to its power of resisting abrasion, and for many purposes this power is the important factor.

Hardness being, as indicated above, a somewhat indefinite term, it is not possible to give any precise statement as to the influence of chemical composition upon the hardness of glass. In general

terms it may be said that glasses rich in silica and lime will be found to be hard, while glasses rich in alkali, lead or barium are likely to be soft. It must, however, be borne in mind that rapid cooling, or even the lack of careful annealing, will produce a very great increase of hardness in even the softest glasses. The actual behaviour of a given specimen of glass will, therefore, depend upon the nature of the processes which it has undergone as well as upon its chemical composition.

The Thermal Properties of Glass, although not of such general importance as the mechanical properties, are yet of considerable interest in a large number of the practical uses to which glass is constantly applied. Perhaps the most important of these properties is that known as thermal endurance, which measures the amount of sudden heating or cooling to which glass may be exposed without risk of fracture; the chimneys employed in connection with incandescent gas burners, miner's lamp chimneys, boiler gauge glasses, laboratory vessels, and even table and domestic utensils are all exposed at times to sudden changes of temperature, and in many cases the value of the glass in question depends principally upon its power of undergoing such treatment without breakage. The property of "thermal endurance" itself depends upon a considerable number of more or less independent factors, and their influence will be readily understood if we follow the manner in which sudden change of temperature produces stress and, sometimes, fracture in glass objects. If we suppose a hot liquid to be poured into a cold vessel, the first effect upon the material of the vessel will be to raise the temperature of the inner surface. Under the influence of this rise of temperature the material of this inner layer expands, or endeavours to expand, being restrained by the resistance of the central and outer layers of material which are still cold; the result of this contest is, that while the inner layer is thrown into a state of compression, the outer and central layers are thrown into a state of tension. Accordingly, if the tension so produced is sufficiently great, the outer layers fracture under tension and the whole

vessel is shattered by the propagation of the crack thus initiated. From this description of the process it will be seen that a high coefficient of expansion and a low modulus of elasticity will both favour fracture, while high tensile strength will tend to prevent it. The thermal conductivity of the glass will also affect the result, because the intensity of the tensile stress set up in the colder layers of glass will depend upon the temperature gradient which exists in the glass; thus if glass were a good conductor of heat it would never be possible to set up a sufficient difference of temperature between adjacent layers to produce fracture; for the same reason, vessels of very thin glass are less apt to break under temperature changes than those having thick walls, since the greatest difference of temperature that can be set up between the inner and outer layers of a thin-walled vessel can never be very considerable. It also follows from these considerations that if a cold glass vessel be simultaneously heated or cooled from both sides, it can be safely exposed to a much more sudden change of temperature than it could withstand if heated from one side alone; on the other hand, when very thick masses of glass have to be heated, this must be done very gradually, as a considerable time will necessarily elapse before an increment of temperature applied to the outside will penetrate to the centre of the mass. It should also be noted here that in addition to the thermal conductivity of the glass, its heat capacity or specific heat also enters into this question, since heat will obviously penetrate more slowly through a glass whose own rise of temperature absorbs a greater quantity of heat. It will thus be seen that "thermal endurance" is a somewhat complicated property, depending upon the factors named above, viz.: coefficient of expansion, thermal conductivity, specific heat, Young's modulus of elasticity, and tensile strength.

The coefficient of thermal expansion varies considerably in different glasses, and we can here only state the limiting values between which these coefficients usually lie; these are 37×10^{-7} as the lower, and 122×10^{-7} as the upper limit. These figures

express the cubical expansion of the glass per degree Centigrade, the corresponding figures for steel and brass respectively being about 360×10^{-7} and 648×10^{-7} respectively. It is interesting to compare with these figures the corresponding value for pure vitreous silica, which, between 0° and 100° C. is 15×10^{-7}. It should be noted that vitreous bodies of extremely low expansibility are obtainable by the suitable choice of ingredients, but in some cases these "glasses" are white opaque bodies, and in all cases they present great difficulty in manufacture, owing to the fact that alkalies and lime must be avoided in their composition.

Quite apart from the question of thermal endurance, the expansive properties of glass are of some importance. Thus, when several kinds of glass have to be united, as, for example, in the process of producing "flashed" coloured glass, it is essential that their co-efficients of expansion should be as nearly as possible the same; otherwise considerable stresses will be set up when the glasses, which have been joined at a red heat, are allowed to cool. On the other hand, this mutual stressing of two glasses owing to differences in their thermal expansion has been utilised for the production of tubes and other glass objects possessing special strength. If a tube be drawn out of glass consisting of two layers, one considerably more expansible than the other, and the cooling process be rightly conducted, it is possible to produce a tube in which both the inner and outer layers of glass are under a considerable compressive stress. Not only is glass, as we have seen above, enormously stronger as against compression than it is against tension, but glass under compressive stress behaves as though it were a much tougher material, being less liable to injury by scratches or blows. Moreover, if a tube in this condition be heated and then exposed to sudden cooling, the first effect of the application of cold will be a contraction of the surface layers, resulting in a relief of the initial condition of compression. These tubes are, therefore, remarkably indifferent to sudden cooling, although they are naturally more sensitive to sudden heating. In this respect they differ entirely from ordinary

glass, which is considerably more sensitive to sudden cooling than to sudden heating, particularly when the heat or cold is applied to all the surfaces of the object at the same time. Special tubes made of two layers of glass in this manner have been manufactured for special purposes, among which boiler gauge glasses are the most important. It should also be mentioned here that the remarkable thermal endurance of vitrified silica, which can be raised to a red heat and then immersed in cold water without risk of breakage, is chiefly due to its very low coefficient of expansion.

In another direction the expansive properties of glass are of importance wherever glass is rigidly attached to metal. At the present time this is done in several industrial products, such as incandescent electric lamps and "wired" plate glass. In certain varieties of incandescent lamps, metallic wires are sealed into the glass bulbs, and the only metal available for this purpose, at all events until recently, has been platinum, whose coefficient of expansion is low as compared with most metals, and whose freedom from oxidation when heated to the necessary temperature makes it easy to produce a clean joint between glass and metal. The use of certain varieties of nickel steel has been patented for this purpose, since it is possible to obtain nickel steel alloys of almost any desired coefficient of expansion from that of the alloy known as "invar," having a negligibly small expansion compared with that of ordinary steel. By choosing a suitable member of this series a metal could be obtained whose coefficient of expansion corresponds exactly with that of the glass to which it is to be united. The oxidation of the nickel steel when heated to the temperature necessary for effecting its union with the glass presented serious difficulties to the production of a tight joint, and several devices for avoiding this oxidation have been patented. The most effective probably consists in coating the nickel steel with a thin sheath of platinum. In the incandescent electric lamp, although the joint between glass and metal is required to be perfectly air-tight, the two bodies are only attached to one another over a very short

length. In wired plate glass, however, an entire layer of wire netting is interposed between two layers of glass, the wire being inserted during the process of rolling. Here a certain amount of oxidation of the wire is not of any serious importance, as it only appears to give rise to a few bubbles, whose presence does not interfere with the strength and usefulness of the glass; but any considerable difference of coefficient of expansion will produce the most serious results on account of the great lengths of glass and metal that are attached to each other. This factor has been neglected by some manufacturers, with the result that much of the wired glass of commerce is liable to crack spontaneously some time after it has left the manufacturer's hands, while there is also much loss by breakage during the process of manufacture.

Thermal expansion is a vital factor in yet another of the uses of glass. Our ordinary instrument for measuring temperature—the mercury thermometer—is very considerably affected by the expansive behaviour of glass. When a mercury thermometer is warmed the mercury column rises in the stem because the mercury expands upon warming to a greater extent than the glass vessel, bulb and stem, in which it is contained. The subject of the graduations and corrections of the mercury glass thermometer is a very large one and somewhat outside the scope of the present volume; but attention should be drawn in this place to the peculiarities of the behaviour of glass that have been discovered in this connection. One of these is that when first blown the bulb of a thermometer takes a very considerable time to acquire its final volume, the result being, that if a freshly made thermometer is graduated, after some time the zero of the instrument will be found considerably changed, generally in a direction which indicates that the volume of the bulb has slightly increased. By a special annealing or "ageing" process this change can be completed in a comparatively short time before the instrument is graduated. There is, however, a further peculiarity which is prominent in some thermometers, although very greatly reduced in the best modern glasses. This

becomes apparent in a decided change of zero whenever the thermometer has been exposed for any length of time to a high temperature, the zero gradually returning more or less to its original position in the course of time. With thermometers made of glasses liable to these aberrations, the reading for a given temperature depended largely upon the immediate past history of the instrument; but thermometer glasses are now available which are almost entirely free from this defect. In this connection the curious fact has been observed that glass containing both the alkalies (potash and soda) shows these thermal effects much more markedly than a glass containing one of the alkalies only.

The thermal conductivity of glass, except in so far as it affects the thermal endurance, is not a matter of any great direct practical importance, although the fact that glass is always a comparatively poor conductor of heat is utilised in many of its applications, as, for example, the construction of conservatories and hot-houses, although even in that case the opacity of glass to thermal radiations of long wave lengths is of more importance than its low thermal conductivity. Similar statements apply, in a still more marked degree, to the subject of the specific heat of glass.

The *Electrical Properties* of glass are of much greater practical importance, glass being frequently used in electrical appliances as an insulating medium. The insulating properties of glass, as well as the property known as the specific inductive capacity, vary greatly according to the chemical composition of the material. Generally speaking, the harder glasses, *i.e.*, those richest in silica and lime, are the best insulators, while soft glasses, rich in lead or alkali, are much poorer in this respect. In practice, particularly when the glass insulator is exposed to even a moderately damp atmosphere, the nature of the glass affects the resulting insulation or absence of insulation, in another way. Almost all varieties of glass have the property of condensing upon their surfaces a decided film or layer of moisture from the atmosphere, and, as we have seen above, glasses differ very considerably in the degree to which

they display this hygroscopic tendency. The softer glasses are much more hygroscopic than the hard ones, and the resulting film of surface moisture serves to lessen or even to break down the insulating power of the glass, the electricity leaking away along the film of moisture. In the case of appliances for static electricity, where very high voltages have to be dealt with, an endeavour is sometimes made to avoid this leakage by varnishing the surface of the glass with shellac or other similar substance, and this proves a satisfactory remedy up to a certain point.

Although glass at the ordinary temperature is rightly regarded as one of the best insulators, yet at high temperatures, when the glass is in a molten or—more properly—in a mobile condition, it becomes a relatively good conductor of electricity. Its conducting powers when in the mobile liquid state are due to the fact that it acts as an electrolyte, and—if matters are suitably arranged—it can be electrolysed in such a manner as to cause an actual separation of the metallic elements present at the cathode. This property of becoming a fairly good electrical conductor when molten makes it possible to heat glass electrically by the passage of a sufficiently heavy current, and this process is employed practically in certain types of electric furnace. It is, however, surprising to find that glass can begin to act as an electrolyte and can undergo appreciable electrolysis at a temperature as low as 200° C. This has been experimentally proved by Warburg and subsequently by Roberts-Austen, who describes his experiments in the Third Report to the Alloys Research Committee of the Institution of Mechanical Engineers in 1895. The results are so remarkable that a part of the description may be quoted:—"Thick bulbs were blown from barometer tube (of soda glass); and in most of the experiments the glass was electrolysed, using mercury and an amalgam of some metal as cathode and anode respectively. The temperature was from 250° C. to 350° C.; the electromotive force employed was 100 volts; and the current in the case of the sodium experiments averaged about one thousandth of an ampere and was sometimes as high as one

fiftieth of an ampere. . . . In the experiments in which sodium amalgam had been placed in the bulb and pure mercury outside, sodium passed into the mercury to the extent of 0·03 grammes. . . . The passage of the mercury follows the ordinary laws of electrolysis. . . . It is doubtful whether the sodium from the amalgam actually penetrated right through the glass, but there can be no question that it replaced a considerable proportion of the sodium which the glass contained. An attempt to pass potassium through the same glass failed. Gold was then used, both in the form of amalgam and dissolved in metallic lead, but in the latter case the temperature employed was of course higher. No gold was found to have been transmitted through the glass; but the glass employed became coloured by gold, and minute spangles of the metal were found embedded in it." This work of Roberts-Austen confirmed the results of Warburg, who had found that while lithium could be caused to pass electrolytically through a soda glass, potash could not—the difference being ascribed to the fact that lithium has a lower atomic volume than sodium, while potassium has a higher atomic volume. Even in the case of lithium, however, the glass used for the electrolysis became opaque and brittle. Perhaps the most important significance of these facts lies in the obvious conclusion that ordinary glass at so moderate a temperature as 200° C. is sufficiently fluid to act as an electrolyte—a fact which serves to strengthen the view—now almost universally accepted—that glass is essentially a viscous liquid and not a "solid" in the strict sense.

The most valuable and in many ways the most interesting of the properties of glass—its transparency—has not been dealt with as yet, and all mention of this subject has been postponed to the end of the present chapter, because the whole subject of the optical properties of glass will be dealt with more fully in the chapter on optical glass (Chap. XIII.), so that a very brief reference only need be made to the matter here.

There can be no doubt that, in most of its practical applications,

transparency is the fundamental and essential property which leads to the employment of glass in the place of either stronger or cheaper materials. By transparency, in this sense, we wish to include mere translucence also, since very frequently it is as necessary to avoid undisturbed visibility as it is to secure the admission of light. It is indeed hard to find any use to which glass is extensively put into which the function of transmitting light does not very largely enter. Almost the only such example of use is the modern application of opal glass to the covering of walls, and the use—not as yet widely extended—of pressed glass blocks as bricks and paving stones ; in these cases it is the hardness and smoothness of surface that gives to the vitreous body its superiority over other materials, but apart from these special cases, the fact remains that well over 95 per cent. of the glass used in the world is employed for purposes where transmission of light is essential to the attainment of the desired result, either from the point of view of utility or from that of beauty. It is interesting to note that the power of transmitting light is not shared by many solid bodies. Some colloidal organic bodies, such as gelatine and celluloid, possess the property to a degree comparable with glass, while certain mineral crystals, such as quartz and fluor-spar, may even surpass the finest glass in this respect ; while some of the other optical properties of glass are greatly exceeded by such natural substances as the diamond and the ruby. But the very brevity of this list is in itself striking, because it must be borne in mind that transparency by no means constitutes the only common characteristic of vitreous bodies.

Although the transparency of glass is so valuable and indeed so essential a property of that substance, it must be remembered that no kind of glass is perfectly transparent. Quite apart from the fact that of the light that falls upon a glass surface, however perfectly polished, a considerable proportion is turned back by reflection at the surface of entry and again by reflection at the surface of exit from the glass, a certain proportion of light is absorbed during its passage through the glass itself, and the transmitted beam is

correspondingly weakened. In the purest and best glasses this absorption is so small that in any moderate thickness very delicate instruments are required to show that there has been any loss of light at all; but even the best glass, when examined through a thickness of 20 in. or more, always shows the effects of the absorption of light quite unmistakably. In fact, not only does all glass absorb light, but it does this to a different degree according to the colour of the light, so that in passing through the glass a beam of white light becomes weakened in one of its constituent colours more than in the others, with the result that the emergent light is slightly coloured. Thus the purest and whitest of glasses, when examined in very thick pieces, always show a decided blue or green tint, although this tint is quite invisible on looking through a few inches of the glass. The ordinary glass of commerce, however, is far removed from even this approach to perfect transparency. The best plate glass shows a slight greenish-blue tint, which is just perceptible to the trained eye when a single sheet of moderate thickness is laid down upon a piece of white paper. When a sheet of this glass is viewed edgewise, in such a way that the light reaching the eye has traversed a considerable thickness, the greenish-blue tint of the glass becomes more apparent. By holding strips of various kinds of glass, cut to an equal length, close together and comparing the colour exhibited by their ends, a means of comparing the colours of apparently "white" glasses is readily obtained. It will be found that different specimens of glass differ most markedly in this respect. Sheet glass is, as a rule, decidedly deeper in colour than polished plate, but rolled plate is as a rule much greener—the colour of this glass can, in fact, in most cases be seen quite plainly in looking through or at the sheets in the ordinary way.

The question of how far the colour of glass affects the value of the light which it transmits depends for its answer upon the purpose to which the lighted space is to be put. Where delicate comparisons of colour are to be made, or other delicate work involving the use of the colour sense is to be carried on, it is essential that all colouration

of the entering daylight should be avoided, and the use of the most colourless glass obtainable will be desirable. Again, in photographic studios it is important to secure a glass which shall absorb as small a proportion of the chemically active rays contained in daylight as possible, and special glasses for this purpose are available. Although for the present the price of these special glasses may prove prohibitive for the glazing of studio lights, their use is found highly advantageous where artificial light is to be used to the best advantage. On the other hand, for everyday purposes, the slight tinge of colour introduced into the light by the colour of ordinary sheet and plate glass, or even of greenish rolled plate glass, has no deleterious effect whatever, the majority of persons being entirely unconscious of its presence.

Glass which has been intentionally rendered absorbent for light of certain wave-lengths is employed for special purposes. The whole range of coloured glasses will, of course, fall under this description, but apart from these a whole series of glasses has been developed by the researches of Crookes, the object being to produce a material for spectacle lenses which will protect the eye of the wearer from the harmful effects of very short (ultra-violet) and very long (infra-red) light waves. This is especially important for furnace workers, such as those employed in glass manufacture, whose eyesight suffers from continued exposure to the radiation of molten glass. Crookes has obtained remarkable results by the introduction of the oxides of the rare-earth elements, notably ceria, into his glasses, some of which, while so slightly tinted as to be scarcely notable, yet afford very considerable protection to the eye. For other purposes, such as observers at sea or in aeroplanes, who are obliged to face the glare of the sun and of its reflection in the water, deeply tinted glasses are employed.

Another purpose for which glass intentionally rendered absorbent for ultra-violet light is sometimes employed with great advantage is the protection of valuable objects from fading or other deterioration resulting from prolonged exposure to strong light. Such

exposure of valuable objects occurs both in the rooms of private houses and in museums and picture galleries. The glazing of such places with glass which—without being unpleasantly tinted—yet absorbs the greater part of the ultra-violet rays would undoubtedly effect a great reduction in the rate of deterioration of exposed objects, since it has been shown that ultra-violet light, although not the sole cause of this kind of fading, is certainly one of the most important and active factors in the process.

Further consideration of the subject of the transmission of light by glass, its absorption, refraction, dispersion, etc., are, however, best grouped together as the "optical" properties of glass, and under that heading they will receive a fuller treatment in connection with the subject of the manufacture of glass for optical purposes.

CHAPTER III

THE RAW MATERIALS OF GLASS MANUFACTURE

THE choice of raw materials for all branches of glass manufacture is a matter of vital importance. As a rule all "fixed" bodies that are once introduced into the glass-melting pot or furnace appear in the finished glass, while volatile or combustible bodies are more or less completely eliminated during the process of fusion. Thus, while the chemical manufacturer can purify his products by filtration, crystallisation, or some other process of separation, the glass-maker must eliminate all undesirable ingredients before they are permitted to enter the furnace, and the stringency of this condition is increased by the fact that the transparency of glass makes the detection of defects of colour or quality exceedingly easy. For the production of the best varieties of glass, therefore, an exacting standard of purity is applied to the substances used as raw materials. As the quality of the product decreases, so also do the demands upon the purity of raw materials, until finally for the manufacture of common green bottles, even such very heterogeneous substances as basaltic rock and the miscellaneous residues of broken, defective and half-melted glass forming the refuse of other glassworks may be utilised more or less satisfactorily.

For the best kinds of glass the most desirable quality in raw materials is thus as near an approach to purity as possible under commercial conditions, and next to that, as great a constancy of composition as possible. For instance, the quantity of moisture contained in a ton of sand appreciably affects the resulting composition of the glass, and if the sand cannot be obtained perfectly dry, it should at least contain a constant proportion of moisture, otherwise it becomes necessary to determine, by chemical tests,

the percentage of moisture in the sand that is used from day to day, and to adjust the quantity used in accordance with the results of these tests, a proceeding which, of course, materially complicates the whole process. In other cases, variable composition is not so readily allowed for, and uncontrollable variations in the composition of the glass result—at times the quality falls off unaccountably, or the glass refuses to melt freely at the usual temperature. The systematic employment of chemical analysis in the supervision of both the raw materials and of various products will frequently enable the manufacturer to trace the causes of such undesirable occurrences; but however necessary such control undoubtedly is, it cannot entirely compensate for the use of raw materials liable to too great a variation in composition or physical character. For not only the chemical composition but also the physical condition and properties of the material are of importance in glass manufacture. Thus it is essential that materials to be used for glass-melting should be obtainable in a reasonably fine state of division, and in this connection it must be remembered that both exceedingly hard bodies and soft plastic substances can only be ground with very great difficulty. Further, where a substance occurs naturally as a powder, this powder should be of uniform and not too fine a grain, more especially if it belongs to the class of refractory rather than of fluxing ingredients. In that case the presence of coarser grains will result in their remaining in the undissolved state in the finished glass, unless excessive heat and duration of "founding" be employed to permit of their dissolution. This applies chiefly to siliceous and calcareous ingredients, but hardened nodules of salt-cake may behave in a similar manner.

A further consideration in the choice of raw materials is facility of storage. Thus limestone in the shape of large lumps of stone which are only ground to powder as required, is readily stored, and undergoes no deleterious change even if exposed to the weather; on the other hand, sulphate of soda (salt-cake), if stored even in moderately dry places, rapidly agglomerates into hard masses,

at the same time absorbing a certain percentage of moisture. Such properties are not always to be avoided, salt-cake for example being an indispensable ingredient in many kinds of glass-making, but the value of a substance is in some cases materially lessened by such causes.

The raw materials ordinarily employed in glass-making may be grouped into the following classes :—

(1) Sources of silica.
(2) Sources of alkalies.
(3) Sources of bases other than alkalies.

(1) *Sources of Silica.*—The principal source of silica is sand. This substance occurs in nature in geological deposits, often of very considerable area and depth. These deposits of sand have always been formed by the disintegration of a siliceous rock, and the fragments so formed have been sifted and transported by the agency of water, being finally deposited by a river either in the sea (marine deposits) or in lakes (lacustrine deposits), while the action of water, either during transport or after deposition, has frequently worn the individual particles into the shape of rounded grains.

In consequence of this origin the chemical composition of sand varies very greatly with the nature of the rock whose denudation gave rise to the deposit. Where rocks very rich in silica, or even consisting of nearly pure silica, have been thus denuded, the resulting sand is often very pure, deposits containing up to 99·9 per cent. silica being known. More frequently, however, the sand contains fragments of more or less decomposed felspar, and smaller quantities of many other minerals, which introduce alumina, iron and alkalies into its composition. Finally, " sands " of all ranges of composition from the pure varieties just referred to down to the clay marls, very rich in iron and alumina, are known.

For the best varieties of glass, viz., optical glass, flint glass and the whitest sheet-glass, as well as for the best " Bohemian " glass, a very pure variety of sand is required, preferably containing less

than 0·05 per cent. of iron, and not more than 0·05 per cent of other impurities such as alumina, lime or alkali. As a matter of fact, sands containing so little iron rarely contain any other impurity except alumina in measurable quantities. The best-known deposit of such sand in Europe is that at Fontainebleau, near Paris, but equally good sand is found at various places in Germany and Austria. The study of British resources in glass-making sands has been taken up with great energy during recent years, and an exhaustive memoir on the subject has been prepared by Professor P. G. H. Boswell. From the account there given it appears that there is at least one very promising British source of pure silica situated at Muckish Mountain, Co. Donegal, but this is rather of the nature of a crushed friable rock than a true sand. This material, however, appears to be sufficiently pure—if the quality can be maintained when exploitation on the large scale is attempted—to be used for the highest grades of glass. Samples and correspondingly good analyses can also be obtained from many other British sources which suggest satisfactory possibilities, and experiments to utilise such sands for good qualities of glass have been made, in some instances with the promise of success. The real test, however, is that of continued uniformity of satisfactory quality over long periods of commercial exploitation. In many cases careful washing or even treatment with dilute acid would effect very material improvement, but it has been rightly pointed out that the cost of sand for most purposes must be kept so low that little margin remains for the careful treatment of the material at the pit or during transport. It follows from this consideration that a sand deposit which is naturally pure and uniform will—even if under the disadvantage of a greater distance—render competition by less-favoured deposits very difficult. The real importance of finding a home source of supply of sand for high-quality glass has, however, been realised, and thanks to the work of Boswell progress in that direction may be confidently expected. A detailed account of the various sand deposits and their characteristics cannot

be given here, and the reader is referred to Boswell's original memoir.

Next in order of value to these exceedingly pure sands, come the glass-making sands of Belgium, notably of Epinal. These usually contain from 0·2 to 0·3 per cent. of iron and rather more alumina, but they are used very largely for the manufacture of sheet and plate-glass. When the standard of quality is further relaxed, a large number of sand deposits become available, and the manufacturers of each district avail themselves of more or less local supplies. Finally, for the manufacture of the cheapest class of bottles, sands containing up to 2 per cent. of iron and a considerable proportion of other substances are employed.

Silica, in various states of purity, occurs in nature in a number of other forms than that of sand. By far the commonest of these is that of more or less compact sedimentary rock, known as "sandstone." As far as chemical composition is concerned, some of these stones are admirably suited for making the best kinds of glass, although as a rule a stone is not so homogeneous as the material of a good sand-bed. The stone has the further disadvantage that it requires to be crushed to powder before it can be used for glass-making, and the crushed product is generally a mixture of grains of all sizes ranging from a fine dust to the largest size of grain passed by the sieves attached to the crushing machine. The presence of the very fine particles is a distinct objection from the glass-maker's point of view, so that it would probably be necessary to wash the sand to remove this dust—a process that in itself adds to the cost of the crushed stone and at the same time leads to the loss of a serious percentage of the material. Objections of the same kind apply, but with still greater force, to the use of powdered quartz or flint as sources of silica for the glass-maker; further, these materials are exceedingly hard and therefore difficult to crush, so that their price is prohibitive for glass-making purposes. The use of ground quartz and flint is therefore confined to the ceramic industries in which these substances serve as sources of silica for

both bodies and glazes; in former times, however, ground flint was extensively used in the manufacture of the best kinds of glass, as the still surviving name of "flint glass" testifies.

Minerals of the felspar class, consisting essentially of silicates of alumina and one or more of the alkalies, are extensively used in glass-making and should be mentioned here, since their high silica-content (up to 70 per cent.) constitutes an effective source of silica. As a source of this substance, however, most felspars would be far too expensive, and their use is due to their content of alumina and alkali.

(2) *Sources of Alkali.*—Originally the alkaline constituents of glass were derived from the ashes of plants and of seaweed or "kelp"; in both cases the alkali was obtained in the form of carbonate and was ordinarily used in a very impure form; at the present time, however, the original source of alkali for industrial purposes is found in the natural deposits and other sources of the chlorides of sodium and potassium. At the present time it is not yet industrially possible to introduce the alkalies into glass mixtures in the natural form of chlorides. The principal difficulty in doing this arises from the fact that the chlorides are volatile at the temperature of glass-melting furnaces and are only acted upon by hot silica in the presence of water vapour. Introduced into an ordinary glass furnace, therefore, these salts would be driven off as vapour before they could combine with the other ingredients in the desired form of double silicates.

Alkalies are, therefore, introduced into the glass mixture in less volatile and more readily attackable forms. Of these the carbonate is historically the earlier, while the sulphate is at the present time industrially by far the more important. The *Carbonate of Soda*, or soda ash, which is used in the production of some special glasses, and is an ingredient of English flint glasses, is produced by either of two well-known chemical processes. One of these is the "black ash," or "Le Blanc" process, in which the chloride is first converted into sulphate by the direct action of sulphuric acid, and the sulphate

thus formed is converted into the carbonate by calcination with a mixture of calcium carbonate and coal. The sodium carbonate thus formed is separated by solution and subsequent evaporation. A purer form of sodium carbonate can be obtained with great regularity by the "ammonia soda" process, in which a solution of sodium chloride is acted upon by ammonia and carbonic acid under pressure. Soda ash produced by this process is now supplied regularly for glass-making purposes in a state of great purity and constancy of composition. It is upon these qualities that the great advantages of this substance depend, since its relatively high cost precludes its use except for special kinds of glass, and for these purposes the qualities named are of great value.

For most purposes of glass-making, such as the production of sheet and plate-glass of all kinds, the alkali is introduced in the form of salt-cake—*i.e.*, sulphate of soda. This product is obtained as the result of the first step of the Le Blanc process of alkali manufacture—*i.e.*, by the action of sulphuric acid on sodium chloride; salt-cake is thus a relatively crude product, and its use is due to the fact that it is by far the cheapest source of alkali available for glass-making. There are, however, certain disadvantages connected with its use. The chief of these is the fact that silica cannot decompose salt-cake without the aid of a reducing agent; such a reducing agent is partly supplied by the flame-gases in the atmosphere of the furnace, but in addition to these a certain proportion of carbon, in the form of coke, charcoal or anthracite coal, must be added to all glass mixtures containing salt-cake. The use of a slightly incorrect quantity of carbon for this purpose leads to disastrous results, while even under the best conditions it is not easy to remove all traces of sulphur compounds from glass made in this way. A further risk of trouble arises in connection with salt-cake from the fact that it is never entirely free from more or less deleterious impurities. According to the exact manner in which it has been prepared, the substance always contains a small excess either of undecomposed sodium chloride or of free sulphuric acid,

or the latter may be present in the form of sulphate of lime. A good salt-cake, however, should contain at least 97 per cent. of anhydrous sodium sulphate, and not more than 1·0 per cent. of either sodium chloride or sulphuric acid. While pure sodium sulphate is readily soluble in water, ordinary salt-cake always leaves an insoluble residue, consisting frequently of minute particles of clay or other material derived from the lining of the furnace in which it was prepared, or from the tools with which it was handled; and these impurities are liable to become deleterious to the glass if present in any quantity. The insoluble residue should not exceed 0·5 per cent. in amount, and in the best salt-cake is generally under 0·2 per cent.

Salt-cake possesses certain other properties that make it somewhat troublesome to deal with as a glass-making material. Thus, on prolonged exposure, particularly to moist air, the powdered salt-cake absorbs moisture from the atmosphere and undergoes partial conversion into the crystalline form of "Glauber's Salt," a process which results in the formation of exceedingly hard masses. Ground salt-cake, therefore, cannot be stored for any length of time without incurring the necessity of regrinding, and this accretive action even comes into play when mixtures of glass-making materials, containing salt-cake as one ingredient, are stored. In practice, therefore, salt-cake can only be ground as it is wanted, and its physical properties make it difficult to grind it at all fine, while the dust arising from this process is peculiarly irritating, although not seriously injurious to health.

Potash is utilised in glass-making almost entirely in the form of carbonate, generally called "pearl-ash." Originally derived from the ashes of wood and other land plants, this substance is now manufactured by processes similar to those described in the case of soda, the raw material being potassium chloride derived from natural deposits such as those at Stassfurth. The pearl-ash thus commercially obtainable is a fairly pure substance, but its use is complicated by the fact that it is strongly hygroscopic and rapidly

absorbs water from the atmosphere. Where it is desired to produce potash glasses of constant composition, frequent analytical determinations of the moisture contents of the pearl-ash are necessary, and the composition of the glass mixture requires adjustment in accordance with the results of these determinations.

As a result of the war it has become necessary to find other sources of potash than the Stassfurth deposits. This has been successfully done by the utilisation of the dust from blast-furnace gases and flues. More recently Spanish deposits of potash have developed a new source of supply. On the other hand, the temporary difficulty of obtaining supplies of potash has raised the question whether for glass-making purposes the use of potash is really essential and how far the potash glasses are really different from those in which the corresponding amount of soda is used. It must be admitted that there is a slight difference in favour of the potash glasses for some purposes; certain varieties of optical glass, for instance, do not allow of the replacement of potash by soda, while for certain decorative purposes there is a slight difference of appearance—but in many cases the demand for potash is due to little more than a prejudice on the part of a manufacturer or his workmen.

The alkalies are also introduced into glass in the form of nitrates (potassium nitrate, or saltpetre, and sodium nitrate, or nitre), but although these substances act as sources of alkali in the glass, they are employed essentially for the sake of their oxygen contents. Such oxidising agents are not, of course, added to glass mixtures containing sulphates and carbon, but are employed to purify the mixtures containing alkali carbonates, and more especially to oxidise the flint glasses. Since these substances are only introduced into glass in small quantities, their extreme purity is not of such great importance to the glass-maker, and the ordinary "refined" qualities of both nitrates are found amply pure enough to answer the highest requirements.

A certain number of natural minerals which contain an appreciable

quantity of alkali are sometimes utilised as raw materials for glass manufacture. The most important of these are the minerals of the felspar class already referred to. These, however, contain a considerable proportion of alumina, while all but the purest varieties also contain more or less considerable quantities of iron. While some glass-makers formerly regarded alumina as undesirable, it is now generally accepted that it is for most purposes, and to a limited extent, a valuable constituent, and upon this view the use of felspathic minerals is based. For the cheaper varieties of glass, however, such as bottle glass, felspathic minerals and rocks, such as granite and basalt, are freely used as raw materials. Another mineral in which both alkali and alumina are found is cryolite. This is a double fluoride of soda and alumina, whose properties are particularly valuable in the production of opal and opalescent glasses. As a mere source of alkali, however, cryolite is much too expensive.

(3) *Sources of Bases other than Alkalies.*—The most important of these are lime and lead oxide, the former being required for the production of all varieties of plate and sheet-glass, as well as for bottles and a large proportion of pressed and blown glass, while lead is an essential ingredient of all flint glass. The only other base having any considerable commercial importance in connection with glass-making is barium oxide, while oxide of zinc, magnesia, and a few other substances are used in the manufacture of special glasses for scientific, optical or technical purposes, where glass of special properties is required. The metallic oxides which are used for the production of coloured glass are, of course, also basic bodies. These will be treated in connection with coloured glasses, with the exception of manganese dioxide, which is used in large quantities in the manufacture of many ordinary " white " glasses.

Calcium Oxide (lime) is generally introduced into glass mixtures in the form of either the carbonate or the hydrated oxide (slaked lime). The carbonate may be derived either from natural sources, or it may be of chemical origin, while the hydrate is always obtained

by the calcination of the carbonate, followed by "slaking" the lime thus produced. Natural calcium carbonate occurs in great quantities in the form of chalk and limestone rocks. Both varieties are used for glass-making. Chalk is a soft friable material which is apt to clog during the grinding operations, particularly as the natural product is generally somewhat moist. As regards the greater part of its bulk, chalk is often found in a state of great purity, but it is frequently contaminated by the presence of scattered masses of flint. Chemically this impurity is not very objectionable to the glass-maker, since it merely introduces a small proportion of silica whose presence need scarcely be allowed for in laying down the mixture. On the other hand, if any fragments of flint remain in the mixture when put into the furnace, they prove very refractory, and are apt to be found as opaque enclosures in the finished glass.

Natural limestone can also be obtained in great purity in many parts of the world. It is generally a hard and rather brittle rock that can be readily ground to powder of the requisite degree of fineness. Flint concretions are not so frequently found in this material, but, on the other hand, it is often contaminated with magnesia and iron. The former ingredient, when present in small quantities, tends to make the glass hard and viscous, so that limestone of the lowest possible magnesia content should be used, especially for the harder kinds of glass, such as plate and sheet-glass, etc. The iron contents of the limestone used must also be low where a white glass is required; but since a smaller quantity of limestone is used for a given weight of glass produced than the quantity of sand used for the same purpose, the presence of a somewhat higher percentage of iron is permissible in the limestone as compared with the sand; for the better varieties of glass, however, the iron should not exceed 0·3 per cent. of the limestone.

Slaked lime is sometimes used as the source of lime for special glasses where the process of manufacture renders it desirable to avoid the evolution of carbonic acid gas which takes place when the carbonate is heated and attacked by silica. When slaked lime

is used only the water vapour of the hydrate is driven off, and this occurs at a much lower temperature. For the production of slaked lime, an adequately pure form of limestone, preferably in the form of large lumps, is burnt in a kiln until the carbonic acid is entirely driven off; after cooling, the lime so formed is slaked by hand. The product so obtained is, however, apt to vary both as regards contents of moisture and carbonic acid, which latter is readily absorbed from the atmosphere; the use of this material, therefore, requires frequent analytical determinations of the lime contents and corresponding adjustments of the mixture if constant results are required.

It is possible to introduce lime into glass mixtures in the form of gypsum or calcium sulphate, but the decomposition of this compound, like that of sodium sulphate, requires the intervention of a reducing agent such as carbon, and the difficulties arising from this source in connection with the use of salt-cake are still further increased in the case of the calcium compound. Since limestones of considerable purity are more or less plentiful in many districts, the commercial value of calcium sulphate for glass-making is probably slight.

The Compounds of Barium may best be dealt with at this stage, since they are chemically very closely allied to the compounds of lime just described. Barium occurs in nature in considerable quantities in the minerals known as barytes (heavy spar) and witherite respectively. The former is essentially sulphate of barium, while the latter is a carbonate of barium. The use of the sulphate meets with the same objection here as in the case of calcium sulphate discussed above, except that the barium compound is much more easily reduced and decomposed than the lime compound. The natural mineral witherite is used to a considerable extent in the production of barium glasses, and these have been found capable of replacing lead glasses for certain purposes. On the other hand, for the best kinds of barium glasses, viz., those required for optical purposes, the element is introduced in the form of artificially pre-

pared salts. Of these the most important is the carbonate, commercially described as "precipitated carbonate of barium"; this precipitated compound, however, does not ordinarily correspond to the chemically pure substance, but contains more or less considerable quantities of sulphur compounds. The question whether these impurities are or are not objectionable can only be determined for each particular case, since much depends upon the special character of the glass to be produced. Both the nitrate and the hydrate of barium are commercially available, but they are very costly ingredients for use in the production of even the most expensive kinds of glass; these substances are, however, obtainable in a state of considerable purity, although the hydrate has the inconvenient property of rapidly absorbing carbonic acid from the atmosphere, thus becoming converted into the carbonate.

Magnesia is another glass-forming base that is closely related, chemically, to calcium and barium. This element is usually introduced into glass mixtures in the form of either the carbonate or the oxide. The carbonate occurs in nature in a more or less pure state in the form of magnesite, and by calcination the oxide is obtained. The natural mineral and its product are, of course, by far the cheapest sources of magnesia, but as the element is only used in comparatively small quantities, the artificial precipitated carbonate or calcined magnesia are frequently preferred. Magnesia is only introduced intentionally in notable quantities in special glasses where the properties it confers are of particular value; in ordinary lime glasses this element, as has already been mentioned, is to be regarded as an undesirable impurity.

Zinc oxide lies, chemically, between the bases already discussed on the one hand, and lead oxide on the other. This element is introduced into certain optical glasses, a special "zinc crown" having found some application. Certain kinds of laboratory glassware also contain zinc. Chemically prepared zinc oxide is almost the only form in which the element is used, but the very volatile

character of this substance must be borne in mind when it is introduced into glass mixtures.

Lead is one of the most widely-used ingredients of glass; the glasses containing this substance in notable quantity are all characterised to a greater or less degree by similar properties, such as considerable density and high refractive power, and are classed together under the name "flint glasses." Lead is now almost universally introduced into glass mixtures in the form of red lead, although the other oxides of lead might be employed almost equally well. Red lead is a mixture of two oxides of lead (PbO and Pb_2O_3) in approximately such proportions as to correspond to the formula Pb_3O_4. It is prepared by the roasting of metallic lead in suitable furnaces, where the molten lead is exposed to currents of hot air. The product is obtainable in considerable purity, very small proportions of silica, derived from the furnace bed, and of iron derived from the tools with which the lead is handled, being the principal foreign substances found in good red lead. Metallic lead is, however, sometimes present, and this impurity is difficult to detect by chemical means. Silver would be an objectionable impurity, but owing to the modern perfect methods of de-silvering lead, that element is rarely found in lead products. Analytical control of red lead as used in the glass mixtures, and consequent adjustments of the mixture, are, however, necessary where exact constancy in the glass produced is desired. The reason for this necessity lies in the fact that the oxygen content, and therefore the lead-oxide (PbO) content, varies decidedly from batch to batch, while the material as actually delivered and used frequently contains notable proportions of moisture.

A word should perhaps be said here as to methods of handling red lead on account of the injurious effects which the inhalation of lead dust produces upon the workmen exposed to it. For glass-making purposes it is not feasible to adopt the method employed by potters of first "fritting" the lead and thus rendering it comparatively insoluble and innocuous; even if this were done, the

difficulty would only be moved one step further back, and would have to be overcome by those who undertook the preparation of the frit. The right solution of the problem, in the writer's opinion, is to be found in properly preventing the formation of lead dust, or at all events in protecting the workmen from the risk of inhaling it. Where only small quantities of lead glass are made, and therefore only small quantities of lead are handled and mixed at a time, it is no doubt sufficient to provide the workmen engaged on this task with some efficient form of respirator to be worn during the whole of the time that they are engaged on such work, and to take the further precautions necessary—by way of cleanliness and the provision of proper mess-rooms—to avoid any risk of lead dust either directly or indirectly contaminating their food. Where, however, large quantities of flint-glass are made every day, it is possible and proper to make more perfect arrangements for the mechanical handling and mixing of the lead with the other ingredients by the provision of suitable mixing and transporting machinery so arranged as to be dust-tight. It is only fair to state, however, that partly under their own initiative, partly under pressure from the authorities, glass-makers in this country are complying with these requirements in an adequate manner.

Aluminium.—There are several varieties of glass into which alumina enters in notable quantities, the principal examples being certain optical and many opal glasses, while most ordinary glasses contain this substance in greater or less degree. In the latter the alumina is derived, by the inevitable processes of solution, from the fire-clay vessels or walls within which the molten glass is contained, while in some cases the element is intentionally introduced in small proportions (about 2 per cent. to 3 per cent. of Al_2O_3) by the use of felspar as an ingredient of the mixture. The introduction of alumina in the form of china clay (a relatively pure silicate of alumina) has recently been recommended. This can only be done successfully in very hot furnaces and provided that the china clay is very finely divided and intimately mixed with the batch—other-

wise it is apt to agglomerate and to form insoluble "stones" in the glass.

Where larger proportions of alumina are required, the substance is introduced in the form of the hydrate, which is obtainable commercially in a state of almost chemical purity, but of course at a correspondingly high cost. In opal glasses alumina is derived partly or wholly from felspars, or in some cases from the use of the mineral *cryolite*. This is a double fluoride of aluminium and sodium which is found in great natural masses, chiefly in Greenland. Owing to the high price of this mineral, however, artificial substitutes of nearly identical composition and properties have been introduced and are used successfully in the glass and enamelling industries.

Manganese.—Although the oxides of this element really belong to the class of colouring compounds, they are so widely used in the manufacture of ordinary "white" glasses that it is desirable to deal with them here. The element manganese is most usually introduced into glass mixtures in the form of the per-oxide (MnO_2), although the lower oxide (Mn_3O_4) can also be used. The material ordinarily used is the natural manganese ore, mined chiefly in Russia; the purest forms of this ore consist almost entirely of the per-oxide, but "brown" ores, containing more or less of the lower oxide, are also used with success. These ores always contain small amounts of iron and silica, but provided the iron is not present in any considerable quantity, the value of the ore is measured by the percentage of manganese which it contains. The colouring and "decolourising" action of manganese will be discussed in a later chapter. Certain other substances, which have been suggested as either substitutes for, or improvements upon, manganese for this purpose need only be mentioned here, viz., nickel, selenium and gold.

Arsenic is another substance frequently introduced into "white" glass mixtures. This element is universally used in the form of the white arsenic of commerce (*i.e.*, arsenious acid, As_2O_3) which is obtained in a pure form by a process of sublimation. Owing to

the very poisonous nature of this material, special precautions must be taken in its use for glass making purposes to avoid all risk of poisoning.

Carbon.—As has already been indicated, an admixture of carbon in some suitable form is essential in the case of certain glass mixtures. The carbon for this purpose may be used in the form of either charcoal, coke, or anthracite coal. Of these, charcoal is undoubtedly the purest form of carbon, but it is expensive in this country. Coke varies very much in quality according to the coal from which it has been produced, but it always contains notable proportions of ash rich in iron, and also some sulphur. Anthracite coal can be obtained in a very pure form, containing considerably less ash than that found in most kinds of coke, and this is therefore probably the most convenient form of carbon for this purpose.

Fluorine.—This element is employed in the form of fluorides, usually either calcium fluoride, or the double fluoride of sodium and aluminium already described (cryolite). Artificial compounds, of the nature of fluo-silicates, are also employed. Except for certain optical glasses of very recent introduction, fluorides are solely used for the purpose of rendering glass opaline. They have the disadvantage that their presence in the batch usually causes violent attack upon the fire-clay of the pot in which the melting is carried out.

Boron.—This element is introduced into glass either as borax (sodium bi-borate) or as boric acid; it is present in the glass in the form of compounds or solutions of the oxide (B_2O_3). Its principal use is in optical glasses, where the acid is generally used in the batch. Borax is, however, sometimes used as a softening agent, particularly in coloured glasses in which the colouring oxide has a tendency to render the glass undesirably hard.

Zirconium.—Zirconium oxide or zirconia (ZrO_2) is a very heavy white substance which is extremely insoluble in most fluxes; in the massive state resulting from fusion it offers very considerable resistance to attack by molten glass. In the finely-divided state

resulting from precipitation, however, it can be incorporated in glass mixtures to a considerable extent. The resulting glass may, according to composition and circumstances, be either clear or opal. In the enamelling industry Zirconia is frequently used for the production of opaque white enamels, and is said to offer advantages over tin oxide. Its use for the production of opal glass is not so well established.

CHAPTER IV

REFRACTORIES

The furnaces and crucibles in which the melting of glass is carried out are required to resist prolonged exposure to very high temperatures and must, therefore, be constructed of materials capable of resisting the destructive effects of great heat. Such materials are usually described as "Refractories," although a very large variety of different materials may be comprised under that generic term. The importance of such material to successful glass manufacture, however, can scarcely be over-estimated. In the first place the life of the furnaces and pots plays a most important part in the economy of a glass-works, not only because of the cost in materials and labour entailed by each renewal, but also because of the very serious loss of output which the stoppage of a furnace implies. There is the further factor that during the process of deterioration which precedes the shutting-down of a furnace for repairs there is a constantly increasing loss of efficiency and frequently a deterioration in the quality of glass turned out. Where glass is melted in pots or crucibles the quality of the refractories used in the construction of the pots is of primary importance also from the point of view of the very strong and direct influence which the quality of the pot exerts on the quality of the glass.

The subject of refractories is, however, a very large and complex one, and its technical details are of interest rather to the manufacturer than to the user of glass. The treatment of this subject in the present volume must, therefore, necessarily be confined to somewhat general considerations. The subject, however, is receiving much fresh attention since war conditions have led glass manufacturers and manufacturers of refractories to realise that careful

attention to the scientific study of refractories is essential to the prosperity of their industries. Some consideration of the subject is therefore necessary in this place.

Broadly speaking the refractories used in glass manufacture may be divided into two classes, according as they are or are not exposed to direct contact with molten glass. Those parts of a furnace which are not in contact with glass, such as the arched "crown" or roof and the upper parts of the walls of furnaces, are almost invariably constructed of the material known as "silica brick," while those parts which come into contact with glass, such as pots, tank-blocks, and the lower parts of pot-furnaces, are almost invariably constructed of some kind of "fire-clay." The difference between these two classes of refractories is this, that while "silica brick" consists almost entirely of silica (SiO_2) held together by a very small proportion of other substances, chiefly lime, acting as binders, "fire-clay" consists essentially of a silicate of alumina ($Al_2O_3,2SiO_2$), which is associated, in some cases, with considerable quantities of additional silica and with other substances in smaller proportions. The reason for this sharp differentiation lies in the fact that silica brick is rapidly attacked and dissolved by molten glass, whose contents of alkali or of lead enable it to enter into chemical combination with the silica. Fire-clay, on the other hand, is capable of developing a very considerable degree of resistance to the dissolving action of molten glass, and although very gradual solution constantly takes place, articles made of suitable fire-clay often resist the action of glass for many weeks and—in the case of tank-blocks—even for years. It must not be supposed, however, that the silica brick, even in the crown of the furnace, is immune from chemical attack, since the dust carried in the flame, as well as vapours arising from the molten glass, attack the silica bricks very powerfully, so that their chemical composition after a prolonged run in the furnace differs very widely from pure silica. The character of this chemical attack is, however, entirely different from that which occurs where there is direct contact with molten glass.

The qualities required in the various types of refractories may now be briefly considered. Of these the first essential is the power of withstanding prolonged exposure to high temperatures. The actual temperatures attained in glass-melting furnaces are rarely, if ever, as high as those which are regularly employed in such a process as steel-melting; as a rule, glass-melting furnaces rarely pass beyond a temperature of 1500° C. or at most 1600° C., while in many tank-furnaces the more usual maximum temperature does not exceed 1400° C. With this may be contrasted the temperatures well up to and above 1700° C., which have been observed in steel-melting, and the still higher range of temperature habitually employed in the electric steel furnace. It would thus seem that from the purely temperature point of view the conditions ruling in glass-melting furnaces are not extremely stringent. On the other hand, it must be borne in mind that in this matter time is an important element, and in this respect the glass furnace makes a much more severe demand on its refractories than does a steel furnace. In a continuous tank furnace the full heat is steadily maintained, with only a very short intermission for flue-cleaning at week-ends, for many weeks in succession; such furnaces have been known to work continuously for close on two years. In contrast with such a length of run, the work of a steel furnace is intermittent and relatively short, the maximum life rarely exceeding two months.

At first sight it would seem that in order to secure that a refractory should satisfactorily resist a certain maximum temperature, it should be sufficient if its melting-point lay well above that maximum. Were refractories simple, pure substances in a crystalline state this condition would no doubt be sufficient, but the materials actually used are very far from being pure, simple crystalline solids, and consequently we find that they do not possess any real, definite "melting point" at all, and their passage from a hard, solid body capable of bearing a load to a glassy molten mass flowing under its own weight is gradual and complex. Confining our attention for the moment entirely to fire-clays, the changes which occur during

gradual heating to a very high temperature may be broadly described as follows: In its initial condition the fire-clay consists of a quantity of very infusible substances, viz.: clay substance proper and silica, accompanied by small quantities of much more fusible substances, such as felspar, iron oxide, etc. As soon as the temperature reaches the melting or softening point of the most fusible of these binding or fluxing substances, its particles, disseminated throughout the clay, become liquid and begin to exert a solvent action upon their surroundings. This action makes itself felt at first only upon the other more fusible substances, but the clay substance and silica are also attacked and slowly dissolved. The result of this action, however, is to render the liquid which has already been formed extremely "thick" or viscous, so that at each temperature a limit is reached beyond which the action will not go—or will only go extremely slowly—until the temperature is raised. If a sample of fire-clay which has been heated only to the earlier stages of this process is allowed to cool and is examined by means of a fracture or a cut section, it is found to be still quite porous and there is very little visible sign—except under the microscope—of the formation of the minute amount of glassy material representing that portion which had been liquid while hot. But as the clay is exposed to still higher temperatures the solvent action of the liquid portion increases—the clay shrinks by becoming less porous and more dense as the process continues. A cooled specimen now shows an increasingly dense or "vitrified" fracture and the porosity is much diminished or—in the latest stages—has disappeared entirely, when the clay is said to be fully shrunk. Finally, if the process is continued far enough, by raising the temperature very high indeed, the proportion of liquid to still undissolved solid becomes so high that the whole mass behaves like a fluid and "runs" or, as it is usually termed, "melts." But it will be seen that the melting process has in reality been extremely gradual and that, long before a small piece of the clay would "run" under its own weight, a brick of the same material would have "squatted" if any serious

load had been imposed upon it. The point at which a given material of this kind will "squat" must depend both upon the quantity of liquid present at that temperature and upon how "thick" or viscous that liquid is.

It follows from these considerations, which can be very fully substantiated by a microscopic examination of samples of fire-clays heated to various temperatures, that any attempt to determine the "melting point" of a refractory is entirely vain. Even the form of test frequently used, in which a trial cone of the clay under test is heated together with a small series of standard "Seger" cones and a comparison made as to their relative refractoriness, is not satisfactory because the small cones do not allow of any satisfactory condition of loading under which the material flows when "squatting" occurs, while the effects of viscosity are largely disregarded as a result of very rapid heating.

For practical purposes the really important test of any refractory is its power to bear a definite load at a high temperature. This test requires somewhat more elaborate appliances than the "cone" test, but its indications are extremely valuable in comparing refractories for any particular purpose. The best method of using such a test would be to determine the temperatures at which bricks or other pieces of standard size failed under a series of increasing loads, "failure" being defined as yielding at an appreciable rate. In a less elaborate form two loads are arbitrarily chosen and the temperatures determined at which the material fails under them. The test adopted by the Bureau of Standards, U.S.A., for this purpose requires that fire-bricks of grade "1A" shall withstand a load of 50 lbs. per sq. in. at a temperature of 1350° C., while for grade "1 B" the load is reduced to 30 lbs. per sq. in. at the same temperature. At first sight it might perhaps appear that this "refractoriness under load" test should only be applied to the material intended for use as bricks or blocks in furnace construction, but even in material intended for pots this property is vitally important, since the hot clay must not only bear the load due to

its own weight, but also the very considerable pressure of the molten glass.

From what has been said already it will be evident that the refractoriness of a given material must depend very much upon its chemical composition, and this chemical composition may itself be regarded from two points of view: we have, first, the composition in regard to the fundamental refractories themselves, which, in connection with glass-melting, are almost exclusively silica and its combinations with alumina, and, second, the fluxing impurities present. The relations of silica and alumina are best recognised from the constitutional diagram of the silica-alumina system, which is reproduced in Fig. 1. Here, as we are dealing with two simple, crystalline solids, we have a curve of real melting or freezing —the upper line of the diagram. This falls from well above 2000° C. at the melting-point of pure alumina down to a temperature just above 1600° C. for a mixture consisting of about 87 per cent. of SiO_2 and 13 per cent. of Al_2O_3. There is an intervening break in the curve with a maximum corresponding to the formation of the mineral sillimanite—a mineral which is found in highly "vitrified" fire-clays and in hard porcelain. On the whole, however, the fusibility of the refractory portion of a fire-clay increases steadily with increasing silica-content up to 86 per cent. It may be mentioned that so-called "clay substance" or "Kaolinite"—Al_2O_2 $2SiO_2$—finds no place on this diagram; this means that no such compound separates from fusions of silica-alumina mixtures and, indeed, that compound is known to undergo

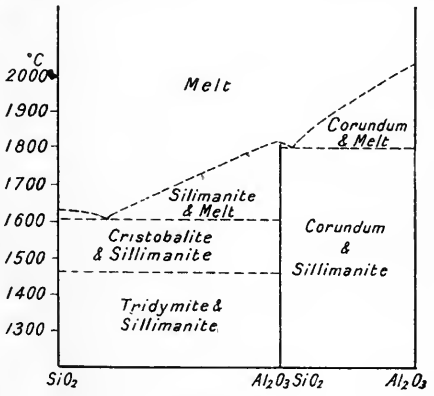

FIG. 1.

decomposition on heating—probably at a temperature between 500° and 600° C., where clay is known to undergo an endothermic reaction on heating. Apart from this, therefore, the refractory value of a fire-clay, disregarding fluxing impurities, might be expressed by its alumina-silica ratio.

In practice, however, fluxing impurities can by no means be disregarded, since it would be useless to have a highly refractory clay basis if it were accompanied by fluxes which would dissolve it at a comparatively low temperature. In this connection it may be noted that alumina is found to be much less readily dissolved in the fluxes ordinarily present than is silica. The fluxes themselves generally exist in the form of felspar (double silicates of alumina and an alkali) and of mica, while iron oxide is always present to some extent. Many attempts have been made to arrive at formulæ by which the refractory value of a clay might be estimated from its analysis in terms of the ratios of silica to alumina and to the sum of the fluxing oxides present, but none of these formulæ possess any great practical value. The only satisfactory way of forming an opinion as to the value of a clay as a refractory is by means of the tests under load at high temperatures. As a matter of interest, however, the chemical analyses of a few typical kinds of refractories used in glass furnaces are here given :—

TYPICAL ANALYSES OF REFRACTORIES.

	—	Silica.	Alumina.	Titanium Oxide.	Ferric Oxide.	Lime and Magnesia.	Alkali.	Loss on Ignition, Water, etc.
	Silica Brick ...	96·62	0·94	—	0·15	1·79	0·50	—
Fire-Clays	Gross Almerode	73·08	15·75	2·10	0·62	0·87	0·43	7·11
	St. Loupe ...	55·40	27·07	2·40	1·02	1·46	0·11	12·47
	Stourbridge 1	66·35	23·50	—	1·54	0·41	—	8·1
	„ 2	73·51	21·89	—	0·53	1·59	—	2·48
	China Clay ...	45·00	40·15	—	0·35	—	0·80	13·70

The power of resisting an adequate pressure at high temperatures, although of fundamental importance, is not the only essential property of refractories intended for use in glass-melting. Besides

resisting the tendency to flow under load, the material must also resist other causes of destruction. One of these takes the form of cracking or flaking, usually termed "spalling," whereby a fire-brick or block is gradually disintegrated. As a rule this form of failure arises from the unequal shrinkage or expansion of different parts of the brick. In the case of silica brick this is liable to be a very serious cause of trouble; in this material it arises from a volume change which occurs when the silica in the brick undergoes the transformation of quartz into tridymite. If the brick has previously been sufficiently severely fired, *i.e.*, if it has been heated long enough and at a sufficiently high temperature during manufacture, this transformation will have been sufficiently completed to avoid risk of cracking so long as the furnace in which the brick is used is not heated—or cooled—unduly quickly. In the case of fire-clay also, if the material is insufficiently burnt, so-called "after-shrinkage" is certain to occur and—if of sufficient magnitude—with disastrous results to the brick and the furnace. Fortunately the condition of a given sample of brick in this respect can be easily tested by exposing it in a suitable experimental furnace to a very high temperature and ascertaining whether it has undergone an undue amount of further shrinkage during this treatment. For tests of this nature the following standards have been suggested: a properly-fired silica brick should not change in volume by more than 1 or 2 per cent. after firing to cone 18, while an adequately fired fire-brick of first-rate material should not shrink by more than the same amount when fired to cone 16. Commercial products unfortunately frequently fail to pass such tests, as there is a considerable tendency on the part of manufacturers to avoid the cost and difficulty of firing their bricks at a sufficiently high temperature. The absolute necessity of doing this must, however, be recognised if the best results are to be obtained. Another test by which the degree of firing to which a given article has been exposed can be approximately ascertained is the measurement of the porosity of the fired materials. This is sometimes measured by weighing the water which the material can

absorb in its pores, or by measuring, in an indirect manner, the amount of air which can be forced into or drawn out of these pores by a given change of pressure. From the brief account given above of the process of vitrification when a fire-clay is heated, it will be seen that diminishing porosity accompanies increasing solution of the clay substance and silica in the fluxes, the full shrinkage resulting from complete vitrification being accompanied by the complete disappearance of porosity. Porosity measurements, however, afford comparable results only on materials of precisely similar composition and cannot be accepted as a general test of quality.

Where refractories are directly exposed to contact with molten glass, the power of resisting solution by the glass is of primary importance. This consideration renders the selection of materials intended for pot-making and for tank-blocks a matter requiring very great care. In the case of tank-blocks the conditions are not so severe as in pots, owing to the fact that the blocks are air-cooled on one side while the other is exposed to the glass. This circumstance lowers the temperature of the fire-clay even where it is in contact with the glass and assists its resistance to solution. In the pot, on the other hand, and more particularly in the closed or covered pot (see below), the heat of the furnace is transmitted to the melting glass through the walls of the pot, so that the fire-clay is, if anything, rather hotter than the glass with which it is in contact. It may be said at once that all ordinary fire-clays are distinctly soluble in molten glass, so that the problem of selection is reduced to finding a clay which shall dissolve as slowly as possible, and as uniformly as possible. Uniformity is particularly important both on account of the quality of the resulting glass—which is apt to be contaminated by particles of clay detached from a pot undergoing irregular attack, and on account of the durability of the pot, which is rendered useless if it is anywhere pierced by a single deep pit, even if it should have remained practically unattacked everywhere else. It is not definitely known upon what factors of composition or constitution uniformity of attack depends, so that

the glass manufacturer can, at present, be guided only by actual trials and experiences of various clays. Generally speaking, however, the clays richest in alumina are also the most resistant to solution. The precise action, however, varies with the nature of the glass. Experiments recently carried out at the National Physical Laboratory indicate very clearly that one of the most important factors in the attack of molten glass on fire-clay lies in the currents which are set up in the glass as a result of the changes in density which the glass undergoes when either silica or alumina derived from the pot are dissolved in it. Where the density of the glass is lowered by the addition of silica and alumina, the glass close to the sides of the pot flows upwards and fresh glass, not yet laden with dissolved clay material, flows inwards towards the sides of the pot near the bottom and also impinges on the bottom of the pot. The result is relatively rapid attack on the bottom and on the sides near the bottom. At the surface, too, currents are set up—probably by the change in the surface tension of the molten glass resulting from dissolution of clay. If these changes are such as to induce a current of glass to flow towards the walls of the pot from the centre a rapid form of attack occurs where the surface of the glass meets the sides of the pot and a deep groove is formed around the pot at the glass level or "water-mark." The experimental study of these various factors has only been begun as yet, but they open up the possibility of controlling the mutual action of glass and clay, by such means as the use of special linings and other local protecting devices, in such a manner as to keep the glass much freer from clay contamination and also to prolong the life of pots to a very considerable extent.

Another class of properties is required of refractory materials in connection with the various processes which they are required to undergo in the course of manufacture into bricks, blocks and pots. For bricks and pots, perhaps, the principal requirement is that the material shall be capable of being formed, by moulding or pressing, or by the casting process referred to below, into the desired

shapes and that, when dry, it shall be strong enough to be safely handled for the purpose of being placed in the kilns for firing. Practically all fire-clays, and many other refractory materials, can be made to answer these simple requirements—in some cases by the addition of some substance which acts as a temporary binder although it disappears or is destroyed during firing. But for the production of pots, and particularly of covered pots, the conditions are not so simple, and until comparatively recently a considerable degree of plasticity was regarded as absolutely essential in pot-clays. For the casting process, however, plasticity is not required and is, indeed, a decided disadvantage, so that this limitation to

FIG. 2.—Open "pot" or crucible for glass-melting.

FIG. 3.—Covered pot for glass-melting, as used for flint glass and optical glass.

a considerable extent disappears. We will, however, first consider the older and still very widely practised processes of pot manufacture out of plastic clays by hand, either with or without the aid of moulds.

The pots used in glass manufacture are of two kinds, known as open and closed or covered respectively. The open pot is simply a vessel, circular or oval in plan and slightly larger at the top than at the base, as shown in the sketch, Fig. 2; they vary in size, in practice, from a capacity of 2 cwt. up to 3 tons, the larger ones measuring about 5 ft. in diameter at the top. Such open pots have the great advantage of simplicity of construction and are more efficient from the point of view of melting, since the heat of the furnace reaches the glass directly through the open top. On the other hand, they expose the glass to reaction with the furnace gases

and also do not protect it in any way from contamination by dust carried in the flame or by droppings from the roof of the furnace. Formerly, for instance, it was not thought possible to melt "flint" glasses, containing considerable proportions of lead oxide, in open pots owing to the reducing action of the furnace gases on the lead oxide in the glass. It has, however, been demonstrated that this difficulty can be successfully overcome by a suitable control of the flame both as to composition and direction, and good flint glass is now regularly melted in open pots. On the other hand, most optical glass and a good deal of the best flint and other "extra white" glass is still regularly melted in "covered" pots. These covered pots have the shape shown in Fig. 3. Here the simple open pot is covered over with a hood or dome, provided with a snout or opening which is so placed as to communicate with the working opening of the furnace, and through this opening the pot is filled and all manipulations are carried out. The construction of such a covered pot is necessarily a matter of much greater difficulty than in the case of an open pot.

The material for pot-making is first prepared with great care. The proper variety of clay having been selected, it is ground to a fine powder in suitable mills and carefully sieved; with this fine clay powder is mixed, in accurately determined proportions, a quantity of crushed burnt fire-clay. In some works this burnt material is obtained by simply grinding up fragments of old used pots, but the better practice is to burn specially selected fire-clay separately for this purpose. The quantity of such burnt material added to the mixture depends upon the chemical nature and especially on the plasticity of the virgin clay employed; with so-called "fat" or very plastic clays up to 50 per cent. of burnt material is added, but with the leaner clays, such as those of the Stourbridge district in England, very much smaller proportions are used. The object of this addition of burnt material is to facilitate the safe drying of the finished pots and to diminish—by dilution—the total amount of contraction which takes place both when plastic

clay is allowed to dry, and further when the dry mass is subsequently burnt; the burnt material or "grog," having already undergone these shrinking processes, acts both as a neutral diluent and also as a skeleton strengthening the whole mass and reducing the tendency to form cracks.

The virgin clay and grog having been intimately mixed, the whole mass is "wet up" by the addition of a proper proportion of water and prolonged and vigorous kneading, usually in a suitable pug mill. The mass leaves this mill as a fairly stiff, plastic dough, but the full toughness and plasticity of such clay mixtures can only be developed by prolonged storage of the damp mass. In the next stage of the process, the plastic clay is passed to the "pot maker" in the form of thick rolls, and with these he gradually builds up the pots or crucibles from day to day, allowing the lowest parts to dry sufficiently to enable them to bear the weight of the upper parts without giving way. The building of large pots in this way occupies several weeks, and during this time the premature drying of any part of the pot must be carefully avoided. After the completion of the pot, drying is allowed to take place, slowly at first, but more vigorously after a time when the risk of cracking is smaller; when it is taken into use the pot is usually many months old and is thoroughly air-dry. The clay, however, is still hydrated, *i.e.*, contains chemically combined water, and this is only expelled during the early stages of the burning process. This process is carried out in smaller furnaces or kilns placed near the melting furnaces. In these the pot or pots are exposed to a very gradually increasing temperature until a bright red heat is finally attained. This is a delicate process in which great care is required to secure gradual and uniform heating, especially during the earlier stages, otherwise the pots are apt to crack and become useless. Finally, when a bright red heat has been maintained for at least a day, the pots are ready to be placed in the furnace, and this is ordinarily done while both pots and furnace are at a red heat, the pots never being allowed to cool down again once they have been burnt.

Recent practice, recognising the great advantage of harder firing of the pots in reducing porosity and by the formation of sillimanite in the material rendering the pot less liable to attack, tends strongly in the direction of pre-heating pots to a very much higher temperature than the bright red heat formerly used. The kilns or "pot arches" are accordingly constructed so as to allow of higher temperatures being attained, while—after the pot has been placed in the furnace or "set"—the furnace is frequently run to its maximum temperature for a number of hours for the purpose of fully firing the pot before any glass or batch is introduced.

Reference must now be made to the process of producing pots and other refractory objects by means of slip-casting. This process has long been in use for the production of a great variety of objects in the ceramic industries. It consists essentially in preparing the material which is to form the body not as a stiff, tough plastic mass but as a thin mud or sludge, known as a "slip." This slip is poured into a mould made of plaster-of-paris, which is highly porous and sucks up the water of the slip while leaving the suspended solid matter behind as a species of mud-deposit on the inner surface of the mould. In its simplest form, such a mould constitutes a vessel which is filled with the liquid slip; when enough material has been deposited on the walls of the mould as the result of the suction of the plaster, the remaining slip is poured out. The material which is left adhering to the plaster walls of the mould then quickly begins to dry, the water it contains being rapidly sucked away by the plaster. After a short time this drying results in a small shrinkage and, if the shape of the mould is suitable, the clay object —still very soft and tender, but sufficiently coherent—shrinks away from the plaster mould and may be removed and allowed to dry slowly in a suitable place. The mould, if dried at intervals, may be used a large number of times. It will be seen that for this purpose the material to be employed does not require the high degree of plasticity needed for hand-moulding; indeed, high plasticity is a

distinct difficulty, since it causes too great and too rapid a shrinkage during the drying process. On the other hand, a little plasticity, accompanied by a small amount of drying shrinkage, is necessary in order to enable the material to free itself from the mould in which it has been cast. Clays which by themselves are unsuited for slip-casting can, however, be rendered satisfactory by the addition to the slip of certain substances. Thus additions of soda or of silicate of soda render a heavy, thick slip sufficiently fluid to be easily cast. These additions, were they to remain in the clay, would diminish its refractoriness very seriously; fortunately, however, these soluble substances are carried away into the plaster mould and ultimately appear as a fringe of crystals, sometimes called " whiskers," on the outside of the mould.

This slip-casting process, as already indicated, has long found wide application in ceramic industries, but in those uses the whole of the body—which may consist of mixtures of such substances as china-clay, ball clay, finely-ground felspar, and finely-ground quartz —consists of material in an extremely fine state of division, with the result that the " slip " is a smooth-flowing liquid in which there is no serious tendency for the various constituents to separate during the casting process. For the production of refractories, however, an admixture of relatively coarse " grog " is essential—as has already been pointed out—in order to reduce drying and firing shrinkage and to render the final product more resistant to changes of temperature, and the initial difficulty in using the slip-casting process for refractories lay in avoiding the separation of the coarser grog particles, particularly while the slip is entering and standing in the mould. If any such concentration of grog does occur, it leads to unequal contraction either during drying or in firing, and the object cracks. This difficulty has, however, been overcome by a variety of devices, the underlying principle being to accelerate the whole operation to such an extent that settling cannot occur and to introduce the slip into the plaster mould in such a manner as to avoid currents and eddies which would lead to local separation

of the grog. Both tank-blocks and pots are now being commercially produced by this process, particularly in America, and extremely satisfactory results have been obtained, especially in regard to uniformity in the quality of the resulting pots. There is the further advantage that the process admits of the use of much non-plastic material. Thus china-clay—the purest and most refractory of all clays—is rendered available for pot manufacture, and the use of other non-plastic or only slightly plastic materials is rendered possible. In the production of pots with special linings, also, this process is likely to prove very important.

We now turn to the second class of refractory materials used in the construction of glass-melting furnaces, viz., those which are so placed as not to come into contact with molten glass. Here mechanical strength and refractoriness are almost the only considerations, but in the roof-vaults or "crowns" of tank furnaces and also of furnaces in which glass is melted in open pots, there is the further consideration that the material of the bricks used shall not contain notable quantities of any colouring oxide, since small flakes, etc., are apt to drop down into the molten glass, and would thus be liable to cause serious discoloration. Such a material as chrome-ore brick is therefore excluded. As a matter of fact, some form of "silica brick" is in universal use. Bricks of this material, otherwise known as "Dinas bricks" from the place of their first origin, in Wales, consist of about 98 per cent. of silica (SiO_2). Pure silica cannot be baked or burnt into coherent bricks entirely by itself, since it possesses neither plasticity when wet nor any binding power when burnt, but an admixture of about 2 per cent. of lime makes it possible first to mould the bricks when wet and then to burn them so as to form fairly strong, coherent blocks. These are of amply adequate refractoriness for the highest temperatures that can be attained in industrial gas-fired furnaces, and their mechanical strength is sufficient to make it possible to build vaults of considerable span, but on the other hand this material requires very gradual heating and constant watching while the temperature

is rising or falling to any considerable extent; the reason for this difficulty lies in the fact that silica bricks swell very markedly during heating, so that unless a vault built of this material is given room to spread somewhat, it will rise seriously and may even break up completely. This risk is avoided by gradually slackening the tie-bolts that hold the vault together, and correspondingly "taking up the slack" as the vault cools when the furnace is let out. Sudden local heat also has a disastrous effect on this material, producing serious flaking. For positions where intense heat is to be borne, and at the same time mechanical strength is required, silica brick is a most valuable material, but owing to its chemical composition it is rapidly attacked by molten glass or by any material containing a notable proportion of basic constituents, so that the silica bricks can only be employed out of contact with glass.

CHAPTER V

FURNACES

HAVING discussed the materials required for their construction, we may now consider, very briefly, the general design and arrangement of some typical glass-melting furnaces. The oldest and simplest form of furnace is, in effect, simply a box built of fire-brick, in the centre of which stands the crucible, while a fire of wood or coal is placed upon either side. To attain any great degree of heat by such means, however, the size of the box or chamber and especially of the grates in which the fires are maintained must be properly proportioned both to the dimensions of the crucible and to each other. The grates are generally wide and deep, while draught is provided by means of a tall conical chimney which stands over the entire chamber and communicates with it by a number of small openings. In a more refined furnace the chamber itself is double, and the flame, after playing round the crucible in the inside of the chamber, is made to pass through the space between the outer and inner chamber before passing to the chimney or cone. We need not give any greater attention to these primitive furnaces, since they are obsolete at the present time. In modern furnaces the process of combustion is carried on in two distinct stages; the first stage takes place in a subsidiary appliance known as a "gas-producer," where part of the heat which the fuel is capable of generating is utilised for the production of a combustible gas; this gas passes into the furnace proper, either direct, while it is still hot from the producer, or after being conveyed some distance, when it is again heated up by the waste heat of the furnace. In either case the gas is hot when it enters the furnace proper, and there it

meets a current of air, also heated by the aid of the waste heat of the furnace. Hot gas and hot air burn rapidly and completely, and if properly proportioned yield exceedingly high temperatures. Seeing that in this process a part of the heat of combustion yielded by the fuel is generated in a subsidiary appliance and is thus lost to the furnace, it appears at first sight somewhat surprising that this system of firing is very considerably more efficient than the old "direct" system where the whole of the fuel is burnt in the furnace itself. But the advantage arises from the fact that in the newer system the fuel is handled in the gaseous form. This has the advantage, first and most important, that the heat escaping from the furnace in the hot products of combustion (chimney gases) can be transferred to the incoming unburnt gas and air and can thus be returned to the furnace. The manner in which this is accomplished will be considered below, but it may be noted here that in some furnaces the escaping products of combustion are so thoroughly cooled that they are unable to produce an effective draught in the chimney of the furnace. Another advantage of the use of gaseous fuel is the fact that complete combustion can be obtained without the use of so great an excess of air as is required when solid fuels are to be burnt completely. For this reason much higher temperatures can be readily obtained with gaseous fuel, while the pre-heating of both gas and air also facilitates the attainment of high temperatures; further, the great facility with which the flow of either gas or air can be regulated by means of suitable valves, makes it possible to secure much greater regularity in the working of the furnaces. Finally, in modern gas-producers, the amount of sensible heat generated and therefore lost to the furnace, is kept very low, the greater part of the heat set free by the partial combustion of coal in the producer being absorbed by the decomposition of a corresponding quantity of steam into hydrogen and carbonic oxide gas. The gas as it leaves one of these producers is not very hot, and the percentage of heat lost in this way is therefore much smaller than in the older forms of gas-producer.

It is again impossible, within the limits of this chapter, to enter into the details of construction and working of gas-producers. We must content ourselves with saying that most modern producers are of the form of a tower in which a thick bed of fuel is partially burnt and partly gasified under the action of a blast of air mixed with steam. The chemical actions that take place are complicated,

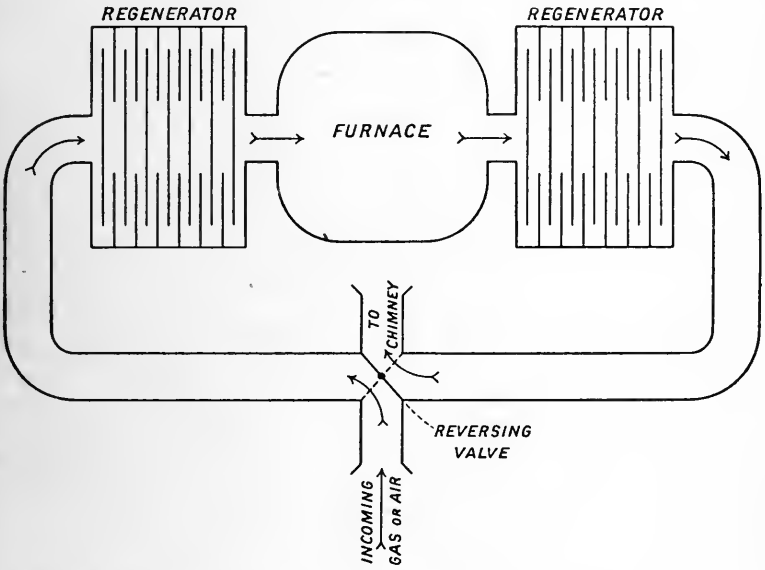

FIG. 4.—Diagram of the arrangements of a regenerative furnace.

but the final result is the production of a gas containing from 2 to 8 or 10 per cent. of carbonic acid, 10 to 20 per cent. of hydrogen, 8 to 25 per cent. of carbonic oxide (CO), 1 to 3 per cent. methane (CH_4), and 45 to 60 per cent. of nitrogen, with varying quantities of moisture, tarry matter, and ammonia. In good producer gas the combustible constituents (hydrogen, carbonic oxide and methane) should total from 30 to 48 per cent. of the whole by volume, but the exact composition to be expected depends very much on the type of producer and the class of fuel used. Some producers are

capable of dealing with exceedingly low-grade fuels, and the gas which they yield can still be utilised for obtaining the highest temperatures—a proceeding that would have been impossible if it had been attempted to burn these fuels directly in the furnace.

The gas on leaving the producer passes along fire-brick flues or passages to the furnace proper; the path which it is now caused to take varies somewhat according to the arrangement of the furnace in question. Modern gas-fired furnaces usually belong to one of two distinct types according to the manner in which the heat of the escaping products of combustion is utilised for heating the incoming gas and air; these two types are known as the "regenerative" and the "recuperative" respectively. In regenerative furnaces the hot products of combustion, after leaving the furnace chamber proper, and before reaching the chimney, pass through chambers which are loosely stacked with fire-bricks; these chambers absorb the heat of the escaping gases, and thus rapidly become hot. As soon as a sufficiently high temperature is attained in these chambers or "regenerators," the path of the gas-currents is altered; the escaping products of combustion are made to pass through, and thus to heat, a second set of regenerating chambers, while the incoming gas and air are drawn through the heated regenerator chambers before entering the furnace proper. The incoming gas and air are thus heated, absorbing in turn the heat stored in the brickwork of the regenerators. It is evident that two sets of such regenerators are sufficient, the one set undergoing the heating process at the hands of the escaping products of combustion, while the other set is giving up its heat to the incoming gas and air; when this process has gone far enough, it is only necessary to interchange the two sets of chambers, by the operation of suitable valves, and this series of alternations may be continued indefinitely. The arrangement is shown diagrammatically in Fig. 4.

In recuperative furnaces the same principle is utilised in a somewhat different manner; the outgoing products of combustion pass through tubular channels formed in fire-clay blocks, while the

ingoing gas and air pass around the outside of these same blocks; the heat of the outgoing gases is thus transferred to the incoming gases by the process of conduction through the fire-clay walls of the recuperator tubes. The arrangement is shown diagrammatically in Fig. 5.

The relative merits of the two systems cannot be definitely stated. While the recuperator as a rule occupies less space and avoids the need for "reversing" valves and their regular attendance, it is more complicated in construction and more liable to get out of order as the result of deterioration in the recuperator blocks or tubes. Defects developing in these parts allow the incoming gas or air to pass direct to the chimney instead of passing through the furnace, so that the efficiency of the furnace becomes seriously impaired. For a considerable period of time the regenerative furnace almost completely monopolised the field, particularly in England, but in recent years a simpler form of recuperator has been introduced and in Sweden and in England a number of successful recuperative furnaces have been installed. Some experimental furnaces at the National Physical Laboratory have been designed on the recuperative principle and have yielded excellent results. Here, however, the recuperator has been made of actual tubes which have been enabled to perform their functions very efficiently by the introduction of silicon carbide (sometimes known as "carborundum") into their composition. It seems probable that large furnaces of this type may prove eminently successful in spite of the somewhat high cost of the material.

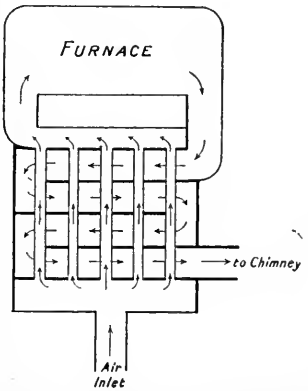

FIG. 5—Diagram illustrating the principle of the recuperative furnace.

In both systems of furnace, heated gas and heated air are admitted to the furnace by separate fire-brick flues or passages, air and gas

being allowed to mix just before they enter the furnace chamber proper. The economy and efficiency of the furnace depend to a very great extent upon the manner in which this mixing is accomplished. Rapid and complete mixing of air and gas results in an intensely hot, but short and local flame, while slower mixing tends to lengthen the flame and spread the heat through the entire furnace chamber; on the other hand, if the mixing of gas and air is too slow, combustion may not have been completed in the short time

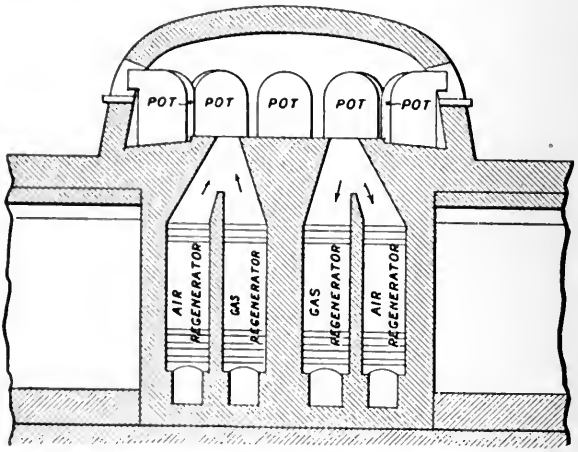

FIG. 6.—Sectional diagram of a regenerative pot furnace working with covered pots.

occupied by the gases in passing through the furnace, and combustion may either continue in the outflow flues and regenerators, or it may be prevented by the narrowness of these passages, and unburnt gases may pass to the chimney. When the openings or "ports" are properly proportioned, and the draught of the chimney is properly regulated, combustion should be just complete as the gases leave the furnace chamber, and under these circumstances small tongues of keen flame will escape from every opening in the furnace; large smoky flames issuing from a gas-fired furnace indicate incomplete combustion.

As has already been indicated, glass is melted either in pots or crucibles of various shapes and sizes, or in open tank furnaces. The general arrangement of a pot furnace working with closed or "covered" crucibles is shown in Fig. 6. In this particular furnace the "ports" or apertures by which the gas and air enter the furnace chamber are placed in the floor of the chamber, but these apertures are often placed in the side or end walls, or even in a central column, the object being in all cases to heat all the pots as uniformly as possible and to avoid any intense local heating, which would merely endanger the particular crucible exposed to it, without greatly aiding the real work of the furnace. In pot furnaces, however, in

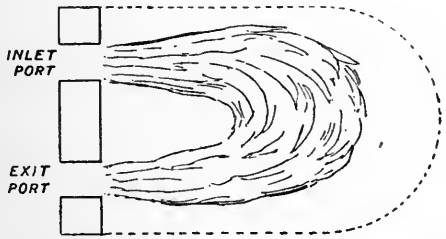

FIG. 7.—Diagram of a furnace with "horse-shoe" flame.

which the more refractory kinds of glass are to be melted, it is generally considered desirable that the flame should be made to play about the pots in such a way as to heat the lower parts of the pots most strongly. In connection with the question of the uniformity of heat distribution in a gas-fired furnace it must further be borne in mind that in the case of regenerative furnaces the direction of the flame is reversed every time the valves are thrown over, and in practice this is done about once every half-hour; this proceeding, of course, tends very much to equalise the temperature of the two sides of the furnace. In recuperative furnaces, on the other hand, the direction of the flame is not changed, and for that reason a flame returning upon itself, usually called a horse-shoe flame, is often employed; this is obtained by placing the entry and exit ports side by side at one end of the furnace; the impetus

of the flame gases and their rapid expansion during combustion carry the flame out across the furnace, while the chimney draught ultimately sucks it back to the exit ports, the shape of the flame being shown in Fig. 7.

In general arrangement a tank furnace for glass-melting resembles an open-hearth steel furnace. The tank or basin is built up of a number of large fire-clay blocks, forming a bath varying in depth from 20 in. to 42 in. according to the design of the furnace and the kind of glass to be melted in it. The ports for entry of gas and air and for exit of the products of combustion are in most modern furnaces placed in the side walls of the furnace just above the

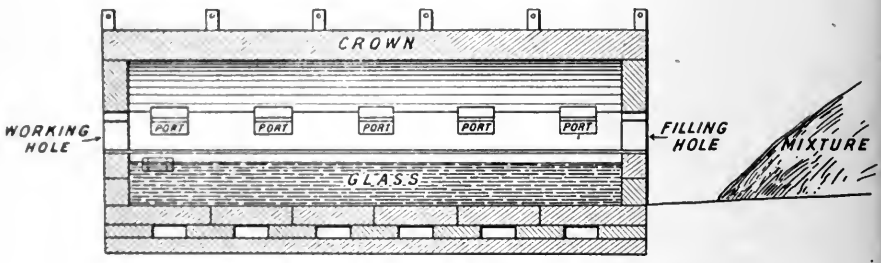

FIG. 8.—Longitudinal sectional diagram of tank furnace.

level of the glass, the whole being covered by a vault built of silica brick. Figs. 8 and 9 show the general arrangement of a simple form of tank furnace such as that used in the manufacture of rolled plate glass. The furnace indicated in the diagram is intended for regenerative working with alternating directions of flame; in recuperative furnaces the horse-shoe flame is always used in tanks, while this arrangement of ports is sometimes adopted for regenerative tanks also, particularly in the manufacture of bottles. For the production of sheet glass, tank furnaces are generally subdivided into two compartments and are also provided with various constrictions intended to arrest impurities and to allow only clear glass to pass, but as regards the arrangement of flues and ports

there is a very general similarity between various furnaces of this type.

Practice has, however, varied very widely in regard to the height of the open space or "flame space" which should be left in a tank furnace above the molten glass. The earliest furnaces were built with a very low "crown" or roof, so that the ports were actually openings in the roof. As a result the flame tended to play directly

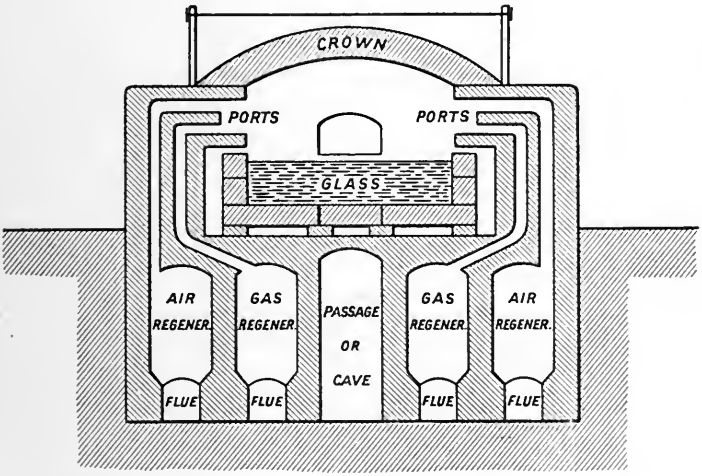

FIG. 9.—Transverse sectional diagram of tank furnace, showing regenerators and gas and air passages.

upon the surface of the glass. Although useful in supplying reducing agents where salt-cake batches were being melted, this arrangement of flame proved unsatisfactory, principally owing to direct contamination of the glass by the flame. A reaction then set in and furnaces with very high roofs were tried, in which the flame played at some height above the glass and the heating of the glass took place largely by radiation from the roof of the furnace. This system proved decidedly inefficient, which is not surprising in view of the fact that the roof is only a relatively thin vault of silica brick which is air-cooled on the outside. Were the furnace built of a non-

conductor of heat—or even of a very poor conductor—its dimensions would be immaterial within wide limits, and the larger internal space would allow of more complete combustion of the gaseous fuel. In practice, however, every square foot of external surface radiates a large amount of heat supplied by thermal conductivity of the walls from the heat of the flame, and it becomes seriously important to reduce external dimensions as far as possible. Modern practice, therefore, both in glass and steel furnaces, tends to keep the crown as low as possible consistent with allowing the flame to sweep just over the surface of the bath and not smothering the flame between furnace roof and bath.

The importance of the point just mentioned, viz., the effect of external surface area of a furnace on its thermal efficiency, affects another important factor of furnace design. This is the thickness of the walls. It would seem, at first sight, that increased wall thickness must lead to increased thermal efficiency by interposing greater resistance to the passage of heat from the interior to the exterior of the furnace. The increase of thickness, however, at the same time increases the exterior surface, and thus—if carried beyond a certain point—actually tends to increase the heat lost from the furnace to its surroundings. The thickness of furnace walls is, however, frequently governed by an entirely different consideration, which is diametrically opposed to the principle of heat conservation by reducing external losses. This consideration arises from the fact that in many cases the refractories used in furnace construction are not good enough to resist the temperature which they would attain if fully exposed to the interior heat; in order to prevent the furnace from collapsing, therefore, it becomes necessary to keep the temperature of the walls from rising too much and for that purpose they are intentionally *air-cooled* by making them relatively very thin. The efficiency of the furnace from the point of view of fuel consumption is thus deliberately sacrificed on account of the weakness, at high temperatures, of the materials used in the construction of the furnace. The extent

to which this occurs in practice can be readily seen by means of a simple experiment. Points can be found on the exterior of most glass-works furnaces where the temperature is low enough to allow the hand to be held against them. If at such a point the surface is covered for a few hours with some bad conductor of heat, such as a brick made of zirconia or of diatomite, it will be found that the wall of the furnace under this covering becomes red hot. This aspect of furnace construction serves to emphasise the importance of a thorough study of refractories and of methods of testing them in order that furnaces may be constructed of materials which do not require such vigorous and wasteful cooling in order to enable them to stand up.

The relative merits of tank and pot furnaces depend entirely upon the character of the glass which the furnace is designed to produce. Wherever the tank can be made to produce glass of adequate quality its great economy inevitably carries all before it, so that bottle glass, for example, is made exclusively in tanks, and the same applies to rolled plate of the ordinary kind and also to the majority of sheet glass. Recently even better grades of glass have begun to be produced in tank furnaces, and special small tanks have come into use of varieties of glass where the output required is not sufficient to justify the continued use of one of the larger types. In some cases, so-called "day" tanks have come into use, in which the furnace runs hot for melting during the night and is then worked out during the day. This mode of working avoids the difficulty of keeping two parts of a small furnace at different temperatures, as would be required if melting and working were to be carried on simultaneously in the way that is done in large tank furnaces.

On the other hand, where special qualities of glass are required in relatively small quantities, or where the requirements as to quality are very stringent, the pot furnace remains indispensable. Optical glass and most coloured glasses are examples of this kind.

The causes of the greater economy of the tank furnace are nume-

rous, and complicated by the detailed requirements of each particular manufacture, but the most important factors in the question may be summed up thus :—

(1) The tank furnace utilises the heat of the flame more efficiently, as the glass is exposed to the heat in a basin whose surfaces covers the entire area of the furnace, while in a pot furnace there is much vacant, unused space.

(2) The tank furnace permits of continuous working, the raw materials being introduced at one end while the glass is being withdrawn and worked at the other end. There are thus no idle periods, and each part of the furnace remains at or near the same temperature during the whole time that a furnace is alight. For a given size of plant, therefore, a tank furnace yields a much larger output, with a relatively smaller fuel consumption.

(3) The tank furnace obviates the need for pots or crucibles, which are not only costly and troublesome to produce, but are liable to premature failure and require periodical renewal, which involves a serious loss of time for the furnace.

(4) Finally, the molten glass in a tank furnace can be always maintained at or near one constant level and is, therefore, always convenient for withdrawal by means of the gatherer's pipe, the ladle, or the blowing machine.

In pot furnaces, on the other hand, the composition of the glass can be more accurately regulated, and the molten glass itself can be more effectively protected from contamination either by matter dropping into it or by the action of the furnace gases, while in pots it is also possible effectually to melt together materials which, in the open basin of a tank, could not be kept together long enough to combine.

CHAPTER VI

THE PROCESS OF FUSION

It has already been indicated that, for glass-making purposes, the raw materials are required in a state of reasonably fine division. The exact degree of fineness required depends very much upon the nature of the ingredient in question, the general rule being that the more refractory and chemically resistant materials require to be most finely ground, while substances which melt and react readily, such as soda ash and salt-cake, do not require very fine grinding.

Assuming that the materials are available in a suitable state of fineness, the first step in the process of glass melting consists in securing their admixture in the proper proportions. This may be done by hand entirely, by hand aided by some machinery, or entirely automatically. The process of hand mixing is only available for relatively small quantities of material and requires very careful supervision if inadequate mixing is to be avoided. In most cases the actual weighing out is done by hand, while the mixing is done by machinery. In this process the separate ingredients are weighed out from barrows or skips and are tipped into a large hopper whence each batch, as soon as it is completed, passes into the mixing chamber of the mixing machine. This may consist of nothing more than a cylindrical chamber in which steel arms revolve and stir up the contents, but more modern appliances take the form of rotating barrels or cylinders, set up on an inclined axis and provided with suitable shelves and baffles; in these the materials are very thoroughly shaken over and mixed. Where hand mixing is adopted, the various ingredients of each batch are thrown into a large bin and are there turned over several times with shovels, the entire

material being ultimately sieved through a wire sieve of suitable mesh. In all cases the resulting mixture should be perfectly uniform in colour and texture, and analyses of different samples should show only small variations. With the mixture thus prepared the "cullet" or broken glass which is to be re-melted is now incorporated; ideally this should also be uniformly distributed, but this is rarely attempted in practice on the large scale.

The next step in the process is the introduction of the mixture into the furnace. In the case of tank furnaces this is a simple matter, since in these the temperature is kept as nearly constant as possible, and raw materials may therefore be introduced at almost any time, the amount introduced being so regulated as to keep the level of the molten glass or "metal" as nearly constant as possible. The actual introduction is managed by means of a large opening or door at what is known as the "melting end" of the furnace. Normally this opening is covered by a large fire-brick block suspended by a chain running over pulleys and counter-balanced by a counterpoise weight. When charging is to begin, this block is raised and the opening is uncovered. The raw materials are then introduced either by hand, by the aid of long-handled shovels, or they are first filled into a long scoop moved by mechanical means forward into the furnace, where it is given a half-turn, which empties the contents out, and is then rapidly withdrawn.

This charging process may be repeated every half-hour, or larger quantities may be introduced once every four hours, according to the practice that may be adopted at any particular furnace.

In the case of pot furnaces the charging process is not so simple. Here the first charge of raw materials has to be introduced into a pot which has been almost entirely emptied during the working-out process, and the temperature of the furnace has also fallen very considerably during this time. Before new material is introduced the heat of the furnace must first be adequately restored. If this is not done, the fusion of the glass takes an abnormal course and very imperfect results arise. Further, the quantity of material

introduced at one time must be carefully adjusted to the capacity of the pot. During the earlier stages of fusion most glass mixtures form large masses of foam, and if the crucible has been too heavily charged this foam overflows, with the result that valuable material is lost and the floor and passages of the furnace are clogged with glass. A certain amount of overflow, as well as leakage from defective crucibles, is, however, unavoidable, and for this purpose every pot furnace is provided with a chamber so placed that the glass will flow into it and so be prevented from finding its way into the regenerators or other parts where its presence would hinder the working of the furnace. These receptacles or "pockets" must, however, be periodically cleared of their contents from outside, and this constitutes one of the most irksome operations connected with glass manufacture. Owing to the occurrence of foaming and to the fact that the raw materials occupy much more space than the glass formed from them, it is necessary to fill the pot with fresh batches of raw materials several times, the quantity which can be introduced decreasing each time. The number of times that this must be done depends upon the particular circumstances, but from four to eight "fillings" are commonly used for various kinds of glass and size of pot. The precise stage at which a fresh batch of raw materials should be introduced is another matter requiring careful attention. For some purposes it is necessary to wait until the previous batch is completely melted, but in other cases raw material may be added whilst some of the previous batch is still floating on the surface of the glass in the pot.

We have now to consider the chemical reactions which take place in the mixture of raw materials that are introduced into the hot furnace. The exact course of these reactions is not known in very great detail, as this could only be ascertained by an elaborate research on the nature of the intermediate products that result under various circumstances. A research of this kind would throw much light on the whole of the melting processes, but is in itself so

difficult that it has not yet been carried out at all fully. We can therefore only give an account of the chemical changes from our knowledge of the end-results and of a few intermediate products that are known. To take the simplest case, we may consider a mixture consisting of sand, carbonate of lime and carbonate of soda mixed in suitable proportions. In such a case we know that the mere action of heat alone will produce two changes—the carbonate of soda will melt and the carbonate of lime will lose its carbonic acid and be "burnt" or converted into caustic lime. The first stage of the fusion process thus probably results in a mass consisting of sand grains and grains of carbonate of lime undergoing decomposition, all cemented together by molten carbonate of soda. This mass will be full of bubbles, some derived from the air enclosed between the grains of the original mixture and thus trapped by the melting mass, and others formed by the carbonic acid which is being driven off in the form of gas by the decomposition of the carbonate of lime. At the temperature of the furnace, however, silica has the properties of a strong acid, and not only attacks the carbonate of lime much in the same manner as, for instance, hydrochloric acid would do in the cold, but the silica also attacks the carbonate of soda, which heat alone can scarcely decompose. The exact order in which these reactions take place will depend upon the temperature of the furnace and the degree of mixing attained in the preparation of the raw materials. Although in the long run the final result will probably be the same as regards purely chemical constitution, much of the technical success of the process must depend upon the exact sequence of the changes involved, as this must govern the number and size of the bubbles that are formed in the glass and the fluidity of the mass from which these bubbles have to free themselves. In the present state of our knowledge, however, we can only say that the final result is the complete expulsion of all carbonic acid from the compounds present (although it may remain entangled in the glass in the form of bubbles) and the formation of silicates of both lime and soda which remain in

the finished glass in a state partly of mutual chemical combination, partly of mutual solution.

The description of the process of fusion just given applies, with slight modifications, to the melting of ordinary flint-glass mixtures as well as to lime glasses, with the one modification that the carbonate of lime of the lime-soda glass is replaced by red-lead, and the gas evolved by the decomposition of the red-lead is oxygen in place of the carbonic acid evolved from the decomposition of the carbonate of lime. In the case of both lime and flint glasses, however, certain other substances besides those mentioned are usually introduced in small quantities. Although these substances do not very materially affect the end-products of the chemical reactions, they very materially affect the intermediate stages, and thus serve the purpose for which they are introduced by affecting the course of the chemical changes in a favourable manner. The substances usually employed for this purpose are arsenic and nitrate of either soda or potash. The manner in which the arsenic acts is very obscure and cannot be discussed in detail here; the chief factors in its action are, however, its volatility and its power of either absorbing oxygen or parting with it according to circumstances. The action of the nitrates is chiefly dependent upon the oxygen which they yield on decomposition by heat. This oxygen is in some cases stored up by other ingredients of the mixture and only given off at a much later stage, when the evolution of this gas assists in the removal of the last small bubbles of inert air or carbonic acid gas still left in the glass. The oxidising action of the nitrates, however, serves chiefly for the destruction of organic matter and the full oxidation of any iron present, both processes which tend to improve the colour of the glass, while in the case of flint glasses the presence of these oxidising additions is necessary to avoid all risk of reduction of lead, since this might result in the complete blackening of the glass, or the formation of metallic lead at the bottom of the pot.

A much more complicated set of reactions occur when the alkali

of a soda-lime glass is introduced either partly or wholly in the form of sulphate of soda (salt-cake). We have already pointed out that the unaided action of heat and of silica is not sufficient to bring about the rapid decomposition of sulphate of soda which is required for successful glass manufacture, and that the intervention of reducing agents is required. For this purpose a certain amount of carbon in the form of coke, charcoal or anthracite coal, is introduced into all salt-cake mixtures, but the reducing gases of the furnace atmosphere also play an important part in the reactions that take place. Here again it is not possible to give anything but an incomplete account of what occurs. The rationale of the whole process lies, no doubt, in the fact that sulphite of soda (Na_2SO_3) is much more readily decomposed by the action of hot silica than the sulphate (Na_2SO_4) itself, so that the essential action of the reducing agents consists in robbing the sulphate of part of its oxygen, thus reducing it to the condition of sulphite and rendering it accessible to the attack of silicic acid. But if we attempt to express such a reaction in the usual manner by a chemical equation from which the quantity of carbon required to effect the reduction in question can be calculated, we find that the amount of carbon required in practice is very considerably less than that given by this theory; it follows therefore that either this very large amount of reducing action must be ascribed to the furnace gases, or that the actual reactions are not strictly of the kind we have described. Both explanations are probably partly correct, and in practice the amount of carbon to be used in a given mixture and furnace can only be found by actual trial, in which the manufacturer is, of course, guided by the results obtained with other furnaces of a similar type. The end-product of the reaction is again a mixture of silicates, while gaseous oxides of sulphur escape from the chimneys of these furnaces in considerable quantities. Some undecomposed sulphate, however, passes into the glass and its presence can always be detected analytically in glass made from salt-cake mixtures. In normal working this sulphate remains in solution in the

glass, but under certain conditions it may separate out in the form of white specks which constitute serious defects in the glass ("sulphate stones"). Analytical control of the sulphate content of the finished glass constitutes one of the most useful ways of controlling the behaviour of salt-cake mixtures.

On the other hand, if too great an amount of carbon is used in the batch or if the furnace gases are excessively reducing, the glass may be discoloured by the presence of alkali or lime sulphide, while in more extreme cases carbon may be present in colloidal suspension, giving rise to colour in the glass ranging from light amber, through deep brown, to black. This colour, however, "burns out" on prolonged melting of the glass.

It is obvious that to a mixture containing carbon as a reducing agent such oxidising materials as nitrates cannot be added, but small quantities of arsenic and of manganese dioxide are added because their other properties are sufficiently valuable to outweigh their disadvantages as oxidising agents.

Having now briefly considered the process of fusion proper, we pass to the second stage in the melting of glass. In a properly conducted glass furnace, when the last trace of undecomposed raw materials has disappeared, we find the glass as a transparent mass throughout which gas bubbles are thickly disseminated. For the majority of purposes it is necessary to free the glass as perfectly as possible from these bubbles before it is worked into its final form. This freeing or "fining" process is carried out by further and more intense heating of the molten glass, which is thereby rendered more fluid and allows the bubbles to disengage themselves by rising to the surface. This occurs much more readily when the bubbles are large; very minute bubbles, in fact, show no inclination to rise through the fluid mass. The glass-maker accordingly compounds his mixtures of raw materials in such a way as to yield large bubbles, or, failing that, he adds to the molten mass some substance that evolves a great many large bubbles, and these in their upward course through the glass sweep the small ones away with them. The

added substance may be an inorganic volatile body, such as arsenic, or more frequently some vegetable substance containing much moisture is introduced into the glass. The most usual method is to place a potato in the crook of a forked iron rod and then to dip the rod with the attached potato into the molten glass; the heat at once begins to drive off the moisture and to decompose the potato, so that there is a violent ebullition of the whole mass. This "boiling up" process assists the fining considerably and also serves to mix the whole contents of the pot very thoroughly, but it has some attendant disadvantages, such as the introduction of oxide of iron into the glass from the rod which is used in the operation, while the contaminated material adhering to the walls of the pot itself is dragged off and mixed with the rest of the glass by the violent stirring action that takes place. It is, of course, further obvious that this process can only be usefully applied to glass melted in pots, since the bulk of the molten glass in a tank furnace could not be reached at all in this manner. Mixtures that are to be melted in tanks must therefore be capable of freeing themselves of their enclosed bubbles without such outside aid. In a tank, in fact, the whole melting process proceeds on somewhat different lines, since the temperature of the furnace is never intentionally varied, while on the other hand the melting glass travels down the furnace into regions whose temperature can be regulated to favour the various stages of the process that take place in each part of the furnace. On the whole, however, it is an undoubted fact that while the running of a pot furnace can be varied, within wide limits, to suit the requirements of whatever mixture it is desired to melt, in the case of tank furnaces the mixture must be closely adjusted to the requirements of the furnace, whose general "run" cannot be very readily altered.

The completion of the "fining" process is generally determined by taking samples of the glass out of the pot or tank and examining them for enclosed bubbles. Such samples may be obtained in a variety of ways, the most usual method being to dip a flat iron rod just below the surface of the glass and to lift it out vertically upwards,

thus retaining on the flat surface of the rod some of the glass that lay there at the moment when the rod was immersed. These test samples or "proofs" are examined very carefully, and if no trace of bubbles can be observed the glass is generally regarded as "fine," but it is by no means certain that the absence of bubbles from such a small sample will prove that the whole mass is free; that, however, is a point where the melter's experience enables him to judge how far he may rely upon the indications given by the "proofs." When the glass is "fine" it frequently happens that the surface of the molten mass is contaminated by specks of foreign matter floating on the glass; for the purpose of removing these, the surface of all glass is skimmed before work is begun upon it. This is done by removing the surface layer of glass by means of suitably shaped iron rods, upon which small masses of molten glass are first "gathered." Finally, it only remains to reduce the temperature of the glass from that of the melting and fining process to the much lower temperature at which the various methods of working the glass are carried out. In pot furnaces this is accomplished by lowering the temperature of the entire furnace, while in tank furnaces the fine glass flows into the working chamber of the tank which is always kept at the working temperature.

CHAPTER VII

PROCESSES USED IN THE WORKING OF GLASS

In the previous chapter we have followed in outline the process of fusion and fining of glass, leaving the molten material ready for working up into the final shape. Up to that point the process is very similar in all kinds of glass, although the furnaces, pots and utensils employed vary considerably, as do also the temperatures to which the materials are heated at various stages. The working processes, however, differ entirely from one class of product to another, as obviously the process employed for the production of a sheet of plate glass can have little in common with that used in the manufacture of a wine-glass. On the other hand, the modes of working hot glass are not so numerous as the products that are produced, so that we find very similar appliances and manipulation recurring in various branches of the industry. For that reason we propose to deal here with the principal methods of manipulating glass, leaving the details of each method as applied to special purposes to be discussed in connection with the special product in question.

The first stage in the working of all glass is the removal of a suitable quantity of molten glass from the furnace. Practically only three methods are available, viz., ladling, pouring and gathering. If we think of a familiar substance having physical properties somewhat resembling those of glass, we may take thick treacle and suppose it contained in a jar or bottle; there are three obvious ways of extracting it from the bottle: we may ladle it out with a spoon, or we may pour it out by tilting the whole bottle, or we may dip a spoon or fork into the thick liquid, slowly draw it out and turn

it round as we do so, thus bringing out on the spoon or fork a round adherent mass or "gathering" of treacle. In the case of molten glass the process of ladling is by far the simplest, but it has certain very decided limitations and disadvantages. These arise from the fact that a ladle cannot generally be introduced into molten glass without contaminating the whole mass of glass, at any rate with numerous air bubbles. The metal of the ladle carries with it a considerable amount of closely adherent air which is partially detached while in contact with the hot glass, so that both the contents of the ladle and the glass remaining in the furnace are contaminated. These bubbles might perhaps be avoided if hot ladles were used, but in that case the glass would adhere to the surface of the metal, and each ladle would require laborious cleaning after each time that it was used. In practice, therefore, ladling is only used for the production of those classes of glass where the presence of a certain number of air-bells is not injurious, and the ladles are kept cold by immersion in water after each time of use. The use of the cold ladle has, however, the further disadvantage that a certain quantity of the glass withdrawn in it is very considerably chilled by contact with the cold metal, and is thus too stiff to undergo the further processes satisfactorily—this chilled glass has, therefore, to be rejected from each ladleful; this not only involves loss of glass, but also necessitates the separation of this spoilt glass from the rest. Where a heavier ladle, made of thicker iron, is used and is allowed to become hotter, a coating or "skull" of glass remains adherent to the ladle after each time of use. This glass, which is liable to be contaminated with oxide derived from the ladle, has to be removed from the ladle and constitutes a loss, although it can be re-melted.

In connection with certain types of glass-blowing machines ladling is used as the means of feeding the glass into the machines. The difficulty arising from the contamination of the glass with air bubbles still remains, but in some cases it has been got over by passing the glass from the ladle into a heated receptacle which

acts as a settling or refining pot in which the glass can rid itself of any bubbles which have been introduced into it. As such bubbles are generally large they rise to the surface quickly, provided that the glass is kept fairly fluid. In this connection it is well to note that glass can be ladled in a much hotter and more fluid condition than that which is necessary for gathering.

The general process of rolling requires little treatment here. Two essentially different processes are used; in one the glass is thrown on a flat table and rolled out by a moving roller passing along the table: in the other the glass passes between two rollers revolving on fixed axes, and the sheet so formed is received on a moving table or slab. The former mode of rolling is used for the production of the ordinary rolled plate glass; if the surface of both table and roller is smooth, the glass also has a comparatively smooth surface, but the surface is far from being level or free from irregularities. It has been found that it is quite impossible to prevent these irregularities, which appear to arise from the buckling of the glass against the iron surfaces with which it comes into contact; when rolled, the glass is too stiff to recover its true, smooth surface under the influence of surface tension, so that it retains all the marks of roller and table—nor can the roller be made *perfectly* smooth, since in that case it appears to slip over the glass and does not roll it out properly. All efforts, therefore, to produce a glass having a true and smooth surface by direct rolling have failed, and are likely to fail, so long as tables and rollers are made of materials similar to those now in use. The process of rolling on a stationary table is, however, used for the manufacture of plate-glass; but here the slab as rolled has still the rough, uneven surface similar to that of ordinary "rolled plate," and this is removed and replaced by a true polished surface by the mechanical processes of grinding and polishing. The second mode of rolling, *i.e.*, with two or more "stationary" rollers and a moving table, is used for the production of rolled plate having special surface features or patterns; the variety of rolled glass known as "figured rolled plate," having a

deeply imprinted pattern, is produced in this way. This method requires much more complicated mechanical appliances, some of which are still protected by patent rights.

Ladling being thus limited to the production of inferior kinds of glass, the better varieties are dependent upon either gathering or pouring. The former process is limited as regards the quantity of glass that can be dealt with in one piece, although surprisingly large quantities can be gathered upon a single pipe; the great masses of glass, however, that are required for the production of modern polished plate could not be handled in this way, and the method of pouring is accordingly adopted. For this purpose either the pots in which the glass has been originally melted, or others specially designed for this purpose, and into which the molten glass has been transferred, are removed bodily from the furnace by the aid of powerful mechanical appliances; they are then carried by overhead cranes to the place where the glass is to be rolled into the form of a plate, and there the pot is tilted and the molten glass is allowed to run out and to form a pool on the rolling table, the passage of the great roller ultimately rolling the pool out into a sheet much as dough is rolled out with a rolling-pin. This process is obviously only possible with pots or crucibles of a suitable size, and is, moreover, very destructive to these pots, since they are exposed to great variations of temperature. In the case of tank furnaces, numerous devices have been patented for allowing the glass to flow out over a sill or weir of suitable size, ready to be rolled or drawn into the form of sheets or slabs; but none of these devices have, so far as the writer is aware, found their way into practice; the reason for this probably lies in the fact that it is not easy to find a material which will present a smooth face to the out-flowing glass, such materials as fire-clay leading to contamination from detached fragments, while chilled metal leads to local chilling of the glass. Although the various processes of drawing glass into sheets direct from the furnace have undergone very material improvement, the laborious process of gathering yet retains its importance

even in the production of such large objects as sheets of window glass.

In its essence the process of gathering consists in introducing into the glass a heated iron rod or tube to which a small quantity of glass is allowed to adhere; rod and glass are removed from the furnace together, and the small adherent ball of glass is allowed to cool so far as to become stiff enough to carry its own weight. The rod with its adherent ball is then again dipped into the glass, where a fresh layer of glass attaches itself to the ball already on the rod. The whole is again withdrawn, allowed to cool down, and then dipped into the molten glass again to gather a fresh quantity. This cycle of operations is repeated until the desired quantity of glass is attached to the rod or tube. These operations, particularly when weights of thirty or forty pounds of glass have to be gathered, require the exercise of a great deal of skill and care; the introduction of the gathering into the molten glass is each time liable to produce air bells which would spoil the whole mass of glass or would contaminate the contents of the crucible, while subsequently the mass of hot glass adhering to the rod or pipe tends to run down and even to drop off entirely if not properly checked by suitable rotation of the pipe. Further, the manual labour and exposure to heat involved for the operator all tend to increase the cost of such work. Mechanical aids to gathering were at first confined to simple devices for relieving the operator of the great weight of the heavier gatherings, but more recently wholly mechanical devices for gathering have come into successful use, particularly in bottle-making. These depend upon suction, the molten glass being drawn up into an inverted cup whose edge is immersed in the glass contained in the furnace. These devices, however, require a special type of furnace or receptacle in which the molten glass is kept at a constant level.

Just as ladling is nearly always preliminary to rolling, so gathering is usually the preliminary to some blowing process, although the blowing is often combined with and sometimes replaced by the

mechanical pressing of the glass. Where the glass is to be blown, the gathering is always made on a glass-maker's pipe. This is an iron tube from 4 to 6 ft. long, provided at one end with a wooden casing to serve as a handle, and with a suitably arranged mouth-piece for blowing. The shape of the lower or "butt" end of the pipe depends upon the character and size of the objects to be blown; for small articles the pipe must be narrow and light, but for heavy sheet glass the butt of the pipe is extended into a conical mass whose base is from 2 to 3 in. in diameter. The bore of the pipe at both ends also depends upon the class of work for which it is intended. At the end of the blowing operation, when the blown article has been detached or "cracked off" from the pipe, a fairly thick mass of glass remains attached to the butt of the pipe. This usually breaks off as it cools, or is readily knocked off, but its value as cullet for re-melting is greatly impaired by the fact that the glass is generally contaminated by adhering layers of iron scale derived from the pipe. For this and other reasons the butts of pipes and of gathering irons are sometimes made of fire-clay, which is formed over the end of the iron tube. In order to secure better adhesion between the clay and the iron, the lower end of the pipe is provided with several pins.

The first stage of all blowing processes consists in the formation of a hollow sphere by blowing into the pipe, the pressure of the breath being as a rule sufficient to cause the gradual distension of the hot mass of glass. From this rudimentary hollow sphere the various shapes of blown articles are then evolved by a series of manipulations which vary very widely in different branches of manufacture. They generally consist, however, in gradually changing the shape of the mass of glass by the pressure either of hand-tools or of specially prepared moulds or blocks against which the glass is held or turned, either with or without simultaneous blowing into the pipe. The extent to which the aid of such moulds and blocks is invoked varies continuously from the production of the hand-made vase or glass to the moulded bottle; in the former,

practically only hand-tools, whose shape bears no direct resemblance to that of the finished article, are employed, while in the latter the elongated hollow mass of glass is placed inside a mould, and internal air pressure is used to press the glass into contact with the mould from which the shape of the finished bottle is thus directly derived.

The art of the blower further takes the fullest advantage of the peculiar physical properties of glass while in the heated viscous condition, the material being made to flow under the action of gravity and centrifugal forces, as well as under the pressure of the breath, the glass being held aloft, twirled or swung about to ensure the production of the various shapes required. For the great majority of such purposes the unaided manipulations of the operator are sufficient, but various mechanical aids are used to facilitate the more laborious stages of the work, while for the simpler forms that are required in very great numbers, such as bottles, the whole of the operations are now carried out by automatic machines. Of the more usual mechanical aids at the disposal of the glass-blower, we have already mentioned hand-tools, blocks, and moulds of various kinds. Next in importance to these is the use of compressed air for blowing large or heavy articles; the pressure available by the human breath is very limited, and the volume of air that can be thus delivered is not very large, while the constant use of the lungs for such a purpose is trying for the workman. In many works, therefore, air under pressure is supplied to the benches or stages where the blowing is done, and the blowers' pipes can be coupled to this air supply by means of flexible connections when required. The principal difficulty lies in the correct regulation of the air pressure for each special purpose; but this difficulty has been overcome by the use of delicate valves under the control of each blower, who can thus regulate the pressure to his own exact requirements. Such a system, of course, requires some little practice on the part of the men using it, but when they have become accustomed to the working of the plant the results achieved are decidedly

better and more regular than those obtained by mouth blowing. Besides the use of compressed air supplied in the way just indicated, several other devices are in use to aid the blower in producing the requisite pressure in the interior of the hollow bodies he is producing. The simplest of all these consists in utilising the expansive force of the air enclosed in the hollow body when that body is exposed to heat. Thus, for instance, in blowing a cylinder of sheet glass, if the blower holds his thumb over the aperture of his pipe, and brings the closed end of the cylinder near the hot "blowing hole," the heat which softens that end of the glass will also act upon the enclosed air, and will very rapidly produce such an expansive effect as to burst open the softened end of the cylinder. This means of opening the closed ends of the cylinder is frequently employed in practice. It is, of course, obvious that any other expansive fluid might be employed in a similar manner, and in some blowing processes it has long been the practice to introduce a small quantity of water into the interior of the hollow body, when the rapid expansion of the steam produced thereby is utilised for the purpose of generating the requisite internal pressure. This use of the expansive force of steam generated by the heat of the hot glass body has been utilised by Sievert, whose process is described in Chapter VIII.

Whatever mechanical aids are employed to facilitate the various stages of the process, all glass blowing involves a series of operations requiring considerable skill, while the whole manner of dealing with the glass is essentially extravagant of material, except perhaps in the production of bottles or flasks having narrow mouths. The reason for this latter statement lies in the fact that by blowing it is only possible to produce closed or nearly closed hollow bodies or vessels; thus a blown wine glass or tumbler is formed with a hood or dome closing in the open top of the glass, and this hood or dome has subsequently to be removed by subsidiary processes, such as cutting off by the aid of strong local heat or by grinding, and the cut edge has to be provided with a smooth finish. In the case of comparatively small articles like glasses the loss involved from

this cause is not so very great, but were large flat bowls or dishes to be produced by blowing, the loss in the dome or covering would be very serious. This difficulty is entirely avoided by the process of pressing glass. We have already indicated the manner in which moulds are used for the production of the desired shape in the case of bottles, etc., but in these cases, where the final object is to be a hollow vessel, the glass is readily forced into contact with the mould by means of internal air—or steam—pressure; in the process to which we are now referring, however, the hot glass is forced into contact with the external mould by means of an internal plunger which is pushed downward with considerable force. By this means flat or shallow bodies can be produced without the preliminary formation of a completely closed vessel, while it is obvious that by the use of suitable moulds, complicated and elaborate shapes can be produced. It is true, of course, that pressed articles do not show the same smooth and brilliant surface which is characteristic of the fire polish of blown articles, while the facility with which elaborate surface ornamentation can be applied by this process has not tended to artistic refinement in design, but the great majority of cheap and useful glass articles of domestic use have been made available by the development of the pressing industry.

In the ordinary course, pressed glass is produced direct from the molten material, which is introduced into the presses either by gathering or by means of ladles, but for some special purposes glass is brought into its final shape by mechanical pressure after having first been allowed to solidify and having then been specially re-heated to undergo the pressing or moulding process. This is principally done in the case of the best kinds of optical glass, where the molten glass is first allowed to cool in the actual crucible and is then broken up into lumps of a suitable size, from which the more defective portions can be rejected, the more perfect portions only being heated up again in special kilns and then forced to take the desired shape by being pressed—sometimes with hand-tools

only and sometimes by the aid of powerful presses—into moulds of the required shape. Small lenses, however, for which the requirements of quality are not so high are sometimes pressed direct from small gatherings taken from the molten glass in the crucible.

In almost every process of glass manufacture the final operation is that of *Annealing*, and although the exact manner in which it is carried out must vary considerably according to the nature of the particular product in question, it may be well in this place to consider the general principles which underlie the operation.

It is, of course, a well-known fact that when glass is either heated or cooled too rapidly it will "fly" or crack. If it is cooled rather more slowly, but still rather fast, it may not crack at the time, but it retains a large amount of internal strain and either cracks spontaneously at a later period or is liable to sudden fracture through small accidental shocks. There is no doubt that much of the apparent great fragility of ordinary cheap glass ware is due to the presence of such internal stresses arising from inadequate annealing. The object of annealing, then, must be the removal—to as complete a degree as possible—of the internal stresses which arise from rapid cooling. To understand how annealing can effect this object we must consider how the internal stresses arise.

Consider, for the sake of simplicity, a spherical mass of glass cooling down from a bright red heat, *i.e.*, from a temperature at which the glass is quite soft. As cooling takes place, the outer layers of the glass will cool down, at first, much more rapidly than the interior. Glass is not a very good conductor of heat, and the outer layers lose their heat so rapidly by radiation and by transmission to the surrounding air that, for a considerable time, the flow of heat from the interior layers of glass is not able to balance the loss. But the flow of heat from the interior increases as the outer layers get colder, so that, after a time, a sort of equilibrium is set up. The temperature difference between inside and outside has then become large enough for the flow of heat outwards nearly (but not quite) to balance the loss of heat from the exterior surface.

During the cooling of any thick piece of glass, then, we must have a difference of temperature set up between the interior and the exterior, and this difference will be larger the faster the rate of cooling and the thicker the piece of glass.

During the cooling process, however, a stage will be reached at which the outer layers have become sufficiently cold to be quite stiff and incapable of adjusting themselves to any forces that may act upon them. At this stage, then, we have a hard "set" outer shell surrounding a much hotter and softer interior mass of glass. Now glass, like the majority of known materials, contracts as it cools, and the greater the range of cooling, the greater also the amount of contraction which takes place. Suppose now that the interior of our sphere of cooling glass is, on the average, 200° C. hotter than the exterior, so that perhaps at one stage in the cooling process the exterior is 200° C. hotter than the surrounding air, while the interior is 400° C. hotter than the air. Ultimately, when the whole mass has cooled down, both exterior and interior must reach the same temperature. In cooling thus, however, the natural contraction of the interior would be something like (although not exactly) double as much as that of the exterior, since it had to cool down through twice the range of temperature. But since the outer layers are hard and stiff, and the interior mass is firmly attached to the outer layers by the natural cohesion of the glass, the interior portions are hindered from undergoing their natural contraction. The result is that a state of tension is set up in the inner layers and a corresponding state of compression in the outer ones. One may think of the inner portion as having first been allowed to contract to the full unhindered extent and then to have been stretched back again to the size of the outer layers by the application of very large tensile forces, and when thus stretched to have been fixed or anchored to the outer layers. Now the actual distance through which the glass has to be stretched thus to undo—or to keep undone—a portion of its natural contraction, is only a very minute one, but it requires the application of exceedingly powerful forces to stretch

solid glass even to so minute an extent. Consequently, if the difference in temperature between outside and inside at the moment when the outer layers become hard has been large, the forces or stresses set up become so large that the glass breaks under them and cracks or "flies." If the difference has been rather smaller, the glass will not actually crack, but remain in a state of severe internal tension. Remembering that the difference of temperature which exists at the critical stage just mentioned depends upon the rate of cooling, we see at once that for the avoidance of internal stresses slow cooling must be adopted, and, further, that the thicker the pieces of glass to be dealt with, the slower must be the rate of cooling employed. It follows, also, that it is the rate of cooling at the critical stage when the outer layers begin to become stiff while the interior is still soft, that really determines the final state of the glass, so that very slow cooling is principally necessary through that critical range.

The simple case we have considered, of a cooling spherical mass of glass, serves to illustrate the principle, but the consideration of another class of case is also instructive. As an example we may take a flat-bottomed tumbler of the type in which the thickness of glass is nearly uniform throughout sides and bottom. Here the actual thickness of glass is nowhere very large and the danger of setting up large differences of temperature between outside and inside layers is not very great unless the glass is cooled very violently indeed. But there is another way in which differences of temperature may arise in such a case, with the resultant setting up of stresses and possible cracking. Suppose the tumbler finished by the blower and at a uniform temperature throughout. If it were now stood upright on a cold slab in such a way as to cool the bottom much faster than the sides, what would result? If at first the sides were still fairly soft the rapid contraction of the bottom, as it cooled down quickly, would draw the sides inwards near the bottom; then, with the bottom perhaps 200° or 300° colder than the sides, the whole would steadily cool. After a time the sides would have

become "set" and stiff, but would still be much hotter than the bottom. Finally, when the bottom was quite cold and would no longer undergo thermal contraction, the sides would still be hot, and during the last stages of their cooling they in turn would contract still further if free to do so. The stiffness of the bottom will prevent this and the ring of glass forming that part of the side wall nearest the bottom would have to remain stretched out to a larger diameter than it would naturally assume after cooling down. This again means that the glass is under a tensile force equal to that which would be required to stretch it mechanically to the size forced upon it by the stiffness of the previously cooled bottom. We would thus have a system of internal stresses very similar in amount, although very different in distribution from those which arise in a thick mass of glass.

The general inference from these examples is that internal stresses will arise in any piece of glass in which widely different temperatures have been allowed to occur during the critical stage of cooling in which one portion is soft while another is already hard. At first sight it would seem that the only way to avoid such stresses would be to secure the most uniform possible cooling of the glass from the moment when its manufacture is finished. As a rule, however, this is not possible; frequently the very success of the manipulation employed in manufacture depends on chilling one part of an article while another is still being moulded. The result is that severe internal stresses are set up in most kinds of glass during manufacture, and it is the object of the annealing operation to remove these as completely as may be necessary for any particular purpose.

Fortunately this can be done, provided only that the stresses set up have not been sufficient to cause actual cracking. If the strained glass is heated up to a temperature at which the whole of the glass is soft enough to yield a very little, and very gradually, to the severe internal forces, then these relieve themselves, and—provided that the subsequent cooling is sufficiently slow and uniform to avoid the occurrence of serious temperature differences within

the glass, the article will come out of the operation relieved of internal stresses or—as it is usually called, "fully annealed." There are two points about the operation, however, which require careful consideration. The first is the temperature to which the glass must be raised in order to allow the strains to be relieved, and the second is the maximum rate of cooling which may be adopted for a given object and a given kind of glass without introducing undue internal stresses. Both can be determined by comparatively simple experiment.

The temperature to which heating should be carried must be high enough to soften the glass to a certain extent but not high enough to soften the glass sufficiently to allow it to become distorted under its own weight. The temperature at which the glass becomes so soft that distortion will occur can be easily determined by placing a rod or tube made of the glass in question in a horizontal tube furnace heated by means of an electric current. The tube or rod is best supported at one end only. As soon as it becomes slightly soft the free end will begin to bend down. This temperature is easily determined by placing a thermo-couple in the furnace, gradually raising its temperature and carefully watching the glass. As soon as the rod or tube begins to bend, the temperature is read, and this reading gives a temperature which is an upper limit which must not be approached during the annealing operation. Generally a temperature at least 50° C. lower is sufficiently high to remove all internal stresses in a few minutes, but the lower limit of temperature can also be determined experimentally, although rather more elaborate appliances are needed.

For this experiment, and also for the testing of finished glass in regard to satisfactory annealing, we depend upon the fact that if polarised light is passed through glass it is not at all affected by its passage so long as there is no stress acting on the glass. If, however, there is internal stress, then the polarised light is affected in a very striking manner. Thus if we look through a tube with a Nicol prism fitted at each end, and the two prisms

are turned into what is known as the "crossed" position, no light passes and we see a black field of view. If glass free from stress is interposed between the two Nicols there is no change, but if strained glass is interposed light is at once seen in the field of view, and this may assume certain well-defined patterns if the glass happens to be strained in a symmetrical manner, and if the stresses are severe we may not only see black and white figures, but vividly coloured patterns make their appearance. It is thus an easy matter to ascertain whether a finished article is or is not fully annealed by examining it between crossed Nicols, or in the similar manner which is described in Chapter XIII. in connection with optical glass.

To apply the test by polarised light to the determination of the annealing temperature it is necessary to place in a little electric tube furnace a block of the glass to be tested, but this block must have its two opposite ends nicely polished. The crossed Nicols are then so placed that the light in passing from the first Nicol (or polariser) to the second Nicol (or analyser) passes through the block of glass under test lying in the furnace tube—in fact, the furnace with the block of glass in it must be placed between the crossed Nicols. When first put into the furnace the block of glass will show patterns—probably coloured—as the result of the presence of internal stresses. Then the temperature of the furnace is very gradually raised and the glass is watched through the crossed Nicols. Gradually, as the annealing temperature is approached, the patterns seen in the glass will begin to change. If—as is frequently the case—these take the form of rings, they will gradually widen out until finally there is perhaps only the trace of one ring left visible near the edges of the block of glass. A very slight further rise of temperature will then remove the last trace of strain, and the full annealing temperature has been reached. Actually, the temperature found will depend upon the rate of heating, but if a reasonably slow rate of heating is adopted the temperature found in the way indicated will be sufficiently accurate as a guide to practice.

With regard to the rate of cooling which can safely be employed, that must depend upon the size and shape of the object, the nature of the glass, and the degree of freedom from strain demanded in the finished article. The requisite rate can best be determined by a series of experiments in which specimen objects are heated to the previously ascertained annealing temperature and cooled at known rates. By examining them in polarised light afterwards it is possible to determine the maximum permissible rate of cooling. It is not, however, essential to carry this slow rate of cooling right down to the ordinary temperature; once the whole of the glass is "set" or stiff, no further internal stresses of a permanent kind can be set up and more rapid cooling can safely be adopted below that temperature. The only limit imposed arises from the risk that the glass may crack as a result of temporary differences of temperature and consequent temporary internal stresses which might be set up by unduly rapid cooling. These temporary stresses arise when any piece of glass is suddenly heated or cooled, owing to the unequal expansions or contractions set up by differences of temperature between different parts. But, provided that no part of the glass is soft when this occurs, all the stresses die out so soon as the glass has attained a uniform temperature. So long, therefore, as the glass is not actually cracked no harm is done by rapid cooling below the point at which the whole of the glass is quite hard.

The methods of arriving at a correct annealing process for any given glass object which have just been outlined may appear complicated to the practical glass-worker who is accustomed to put his products into a "lear" and expects them to come out at the other end properly annealed. But a scientific treatment of the annealing problem is of much greater importance than is sometimes realised. Endless difficulties arise in the practical utilisation of glass products, particularly for technical purposes, which are ultimately traceable to unsatisfactory annealing. This is particularly the case in technical products, but makes itself felt in

domestic usage also. An examination of any large number of glass objects in polarised light reveals a very unsatisfactory state of practice in this respect. Closer attention to the whole matter is therefore of great importance to the progress of the glass industry.

CHAPTER VIII

BOTTLE GLASS

Although bottles are in some respects the cheapest and crudest products manufactured of glass, their uses are so innumerable and their numbers so enormous that their production constitutes a most important branch of the industry.

In the choice of raw materials for the production of ordinary bottles cheapness is necessarily the first consideration. Natural minerals, bye-products of other industries, and the crudest chemicals are utilised so long as it is possible by compounding these ingredients in suitable proportions to obtain a glass whose composition meets the somewhat crude requirements which bottles are expected to meet. The most essential of these requirements are that the bottles shall be strong enough to resist the internal pressure which may come upon them when used for the storage of fermented or effervescent liquors as well as the shock of ordinary use, while the glass itself must possess sufficient chemical resistance to remain unattacked by the more or less corrosive liquids which it is called upon to contain. Further, from the point of view of the bottle manufacturer it is desirable that the glass shall be readily fusible, easily worked, and easily annealed. In other branches of glass manufacture increased fusibility is often attained by increasing the alkali contents of the glass, but in bottle-making this is inadmissible, both on account of the prohibitive cost of alkali and because an increased alkali content renders the glass more liable to chemical attack. On the other hand, in many varieties of bottle the *colour* of the glass is nearly, or quite, immaterial, so that the introduction of relatively large proportions of iron oxide is permissible. This

substance acts as a flux and assists in the production of a fusible, workable glass containing little alkali. Such alkali as bottle glass does contain is frequently derived from felspathic minerals, which generally also contain considerable proportions of iron. The use of these minerals also introduces notable proportions of alumina into the glass. In certain classes of bottles, notably those used for special wines, certain shades of colour are required—the well-known "Hock bottle" colour being an example. The presence of iron in the glass tends to the production of a green or greenish-yellow colour deepening to a black opacity if the quantity of iron be high. The lighter shades of this green tint may be "neutralised" by the introduction of manganese into the glass, the resulting colours ranging from light amber to purple; nickel oxide is also sometimes used as a colouring material in these glasses.

In the production of ordinary bottles the continuous tank furnace has now entirely superseded the old pot furnaces, the character of the product being in this case particularly suited to this process of production. The modern bottle glass tank is generally an oblong basin having one semi-circular end. The flame is often of the "horse-shoe" type, the gases both entering and leaving at the flat or charging end of the furnace. The raw materials are thrown into the furnace at the square end of the tank, and the glass flows uninterruptedly down to the colder semi-circular end where the working holes are situated. At these points fire-clay rings are kept floating on the glass, and from within these the gatherer takes his gathering, the rings serving to retain the grosser impurities carried down by the glass. The producing power of such a furnace, even when the bottles are blown by hand, is very considerable; a furnace having ten working holes and containing normally about 85 tons of molten glass will yield some four million bottles per annum, and furnaces of considerably larger capacity are in use.

The methods of bottle-making are at the present time passing through the later stages of a transition. Up to the middle of last century the processes in use were little better than those of the

middle ages; the first step in a more modern development of the industry took the direction of improved tools and implements for carrying out the old operations. More recently a whole series of inventions have been put forward for producing bottles by entirely different and wholly mechanical processes, eliminating the uncertain element of skilled labour entirely. While it must be admitted that some of the earlier of these inventions proved to be brilliantly ingenious failures, there is little doubt that here, as in other manufacturing processes, the machine-made article will ultimately entirely supersede the hand-made product. Mechanical processes are already in extensive use both in America and Europe, and machine-made bottles are produced which in every point of quality are superior to the best hand-made goods.

The first stage in the production of bottles by hand, and also for most of the machine processes, is that of gathering the requisite quantity of glass. The bottle-blower's pipe is between 5 and 6 ft. long, and is provided with a slightly enlarged end or "nose" upon which the glass is gathered. Three gatherings are generally sufficient for the production of ordinary bottles, but for extra large bottles, and especially for carboys, heavier gatherings are necessary, and for these the gatherer must go the furnace four, five, or even six times. When the requisite quantity of glass has been gathered on the pipe the gathering is worked and rounded by rolling it either on a flat metal plate or "marver," or in a hollowed block made of wood or more rarely of metal; by this process the glass is formed into a well-rounded, symmetrical pear-shaped body. The blower now distends the mass gradually by the pressure of his breath, at the same time swinging the pipe, the effect of these movements being to draw the bulk of the glass downwards, leaving a thinner and colder portion having the rudimentary shape of the neck of the bottle next to the pipe. In the oldest form of the process the next stage in the production of the bottle is accomplished by the aid of a cylindrical mould of fire-clay, whose diameter is that of the external size of the finished bottle. The pear-shaped bulb of

glass is for this purpose re-heated at the melting furnace, and is then placed inside the fire-clay mould. By vigorous blowing, and a rapid rotation of the pipe and glass, the bulb is forced to assume the cylindrical shape of the mould, the glass forming the neck of the bottle being at this stage of the process too cold and stiff to be further deformed. The next step is the formation of the concavity found in the base of wine and beer bottles; this is produced by pushing up the hot plastic glass that forms the bottom of the bottle as it leaves the clay mould. This is done by a second workman using an iron rod known as the "pontil," upon which a small mass of glass has previously been gathered. This mass of glass remains attached to the bottom of the bottle, which is thus for the moment fastened both to the "pontil" and to the blower's pipe. The blower, however, immediately detaches the bottle from the pipe at the point where the neck of the bottle is intended to end, effecting this by locally chilling the glass—a process known by the descriptive term of "wetting off." The unfinished bottle is now attached to and handled by means of the "pontil." The neck is softened by re-heating it over the furnace, and is then moulded into the desired shape by the aid of specially-shaped tongs. Finally a thread of glass is wound round the end of the neck to produce the thickening usually found at that point. The finished bottle, still attached to the "pontil," is now carried to the annealing kiln, where it is placed in position and detached from the "pontil" by a sharp blow, which severs the glass that had been gathered on the "pontil" from the bottom of the bottle.

The process, in the form described above, has been obsolete for many years, improvements, consisting of appliances for facilitating the various operations, having been gradually introduced. The most important of these is the substitution of metal moulds for the fire-clay moulds of earlier times. These metallic moulds are made to open and close at will by the action of a pedal, and are designed to give the entire bottle its final shape, except for the indentation of the bottom, although this is sometimes produced by a convex

piece placed on the bottom of the mould. In the formation of the neck thickening, also, important mechanical aids have become almost universal. These last consist of tongs provided with rollers and arranged to rotate about an axis that terminates in a tapered spike which enters the neck of the bottle; by pressing the tongs together so as to bring the rollers against the outside of the neck and rotating the whole, the rollers are made to form the neck thickening in an accurate and rapid manner.

Important and valuable as these improvements of the ancient process of bottle-blowing undoubtedly are, they do not touch the main disadvantages of the process—disadvantages that seriously affect its economy and the well-being of the workers employed upon it. It is consequently not surprising that a great number of inventors have laboured at the problem of the purely mechanical production of bottles. A large number of patents have accordingly been taken out in connection with bottle-making machinery. The first of these to attain any favour was that devised by Ashley, but although great claims were made for it, its use has not extended. Recently, however, the mechanical blowing of bottles and similar articles has made very great strides, both in England and America. The machines used in England are still mostly of the semi-automatic type, requiring the service of gatherers and operators for various stages of the work. In America, on the other hand, development has reached the stage of the completely automatic machine in which no hand-work is required, the machine taking the molten glass from the furnace and delivering the fully-annealed bottle at the mouth of the lear without manual intervention. Detailed descriptions of these machines cannot be given without elaborate drawings which would lie beyond the scope of the present book. A general account of the mode of operations of bottle-blowing machines is, therefore, all that can be given.

The earlier machines, of which that invented and operated by Boucher, of Cognac, in France, prior to 1900, is one of the most successful examples, closely imitated the process of bottle-blowing

by hand, and this is still the case with many of the semi-automatic machines which operate on the "press and blow" principle. In these machines the glass is taken from the furnace by a gatherer on a gathering-iron (not a tube) and is dropped into the "parison" mould. This mould serves in the first place to limit the amount of glass to the right quantity and also gives the glass its initial shape, *i.e.*, forms it into a "parison." In the earlier machines the "thread" of the glass had to be cut off by hand, but in the newer types this is done by a mechanically-actuated shears or knife. In the "press and blow" machines the first step in the formation of the bottle consists in the piercing and shaping of the interior of the neck by a plunger, which is pressed into the soft glass lying in the neck of the parison mould. This plunger at the same time serves to chill and stiffen the glass of the neck, which then serves as a handle by which the machine holds and manipulates the bottle during the later stages. The only difficulty about this type of machine is that there is a downward limit to the size of plunger which will work satisfactorily for such a purpose, so that for small bottles, with very narrow necks, the plunger becomes too thin and weak. In that case the neck has to be formed by blowing alone, and the glass at and near the neck of the parison is chilled by air blown upon it from the outside. This type of machine is generally known as the "blow" type as distinct from the "press and blow" previously referred to.

The subsequent stages in the formation of the bottle are very similar in all types of machines; the parison is held by the neck and is automatically transferred to a finishing mould in which it is blown to the final shape by compressed air admitted through the previously formed neck. In the more usual semi-automatic machines the bottle is then carried by a boy from the machine to the lear for annealing.

While machines of this type constitute a great advance in economy on the old hand process, they are still far behind the completely automatic machines, of which the Owens machine is probably the

finest example. This machine really comprises a complete special glass-making plant, in which the glass is melted in a special type of tank out of which it flows in a steady stream into a revolving basin or tank in which the glass is maintained at a constant level and at the right working temperature. Close over the surface of the glass in this basin the parison moulds move on their arms and, at suitable intervals, dip their edges into the glass and—by means of suction—fill themselves with glass. When the mould is full it is automatically raised and the glass is cut off by a knife which passes under the mould. The glass, while being sucked into the mould, is already formed into the neck and chilled, so that as the mould moves on, the glass is stiff enough to allow the mould to open, leaving the parison suspended by the neck. At this point compressed air is admitted into the neck opening and simultaneously the finishing mould closes around the parison, which is thus blown into its final shape. A little later the finishing mould opens and the neck of the bottle is released from the hold of the machine. The finished bottle then drops down a chute and passes—again automatically—to a continuous lear through which it is again carried automatically. The finished, annealed bottle is thus produced by entirely automatic means, without human handling at any stage. These machines, originally constructed with six gathering arms, now have as many as fifteen, and a single machine deals with the entire output of a tank-furnace.

It is, of course, obvious that the utility of such machines is not confined to the production of bottles, but that any articles which can be blown in a simple mould can be produced in this way. Lamp-chimneys and electric light bulbs and many other articles come under this heading. For the production of electric light bulbs, however, special machines have been devised. In one of these the molten glass is ladled out of the melting furnace into a special small receptacle or tank in which the glass can be kept at a constant level, but this arrangement has serious disadvantages as compared with the Owens suction gathering device. On the other hand,

some very recent developments tend in the direction of using moulds which are automatically filled by molten glass flowing in a steady stream over a ledge or "weir"—but the details of these devices are not yet publicly known. The output capacity of these automatic machines is, of course, very large; a single machine making electric light bulbs, which are very light, has turned out as many as 18,000 bulbs per twenty-four hours. The automatic machines, however, are equally capable of dealing with very heavy masses of glass, and bottles varying in size from one ounce to one hundred ounces have been produced on the same machine.

The annealing of bottles was formerly carried out in large chambers or kilns of very simple construction, in which the bottles were stacked as made, the kiln being previously heated to the requisite temperature: when full, the kiln was closed up in a rough temporary manner and allowed to cool naturally, thus annealing the bottles stacked within it. In this branch of glass-making also, however, the continuous annealing kiln has superseded the older kinds, and continuous kilns are now almost universal in bottle-making. In these kilns, which consist of long tunnels, kept hot at one end and having a gradually decreasing temperature as the other end is approached, the bottles are stacked on trucks which are slowly drawn through the kiln from the hot to the cold end. At the cold end the trucks are unloaded and are then returned, by an outside route, to the charging end, but of course the bottles cannot be stacked on the truck until it has actually entered the hot end of the tunnel and acquired the temperature there prevailing. In a slightly different form of kiln the bottles are carried down the kiln on a species of conveyer belt formed of iron plates, but the principle of all these appliances is similar even when used for very different kinds of glass.

In the account of bottle manufacture given above we have referred almost exclusively to the mode of production of the ordinary bottles used for the storage of such liquids as wine, beer, spirits, etc., and

we will now deal with some other branches of manufacture closely allied to these.

An important branch of glass manufacture is the production of vessels of large dimensions. Those most closely allied to ordinary bottles are the vessels known as carboys, used for the storage and transportation in bulk of chemical liquids, and especially of acids. Formerly these were blown by hand in a manner closely resembling that used for ordinary bottles, but the weight of the mass of glass to be handled by gatherer and blower is very great, while the lung power of a blower is not sufficient to produce the great expansion required. Formerly the only aid available to the blower was the device of injecting into the hot, hollow glass body, at an early stage of the process, a quantity of water or alcohol; this liquid was immediately vaporised by the heat of the glass, and if the blower closed the mouthpiece end of his pipe by placing his thumb over it, the expansive force of the vapour so generated served to blow out the glass to the desired extent. More recently aids to the production of these large vessels have become available, first in the shape of mechanical arrangements for relieving the workmen of the full weight of the glass and pipe by providing suitable arms upon which the whole can be supported without interfering with the blower's freedom of manipulating the pipe and glass in the desired way; further, a supply of compressed air, which can be readily connected with the pipe at any desired moment, facilitates the blowing process. The newer bottle-blowing machines, however, can also deal with carboys.

A process of producing hollow glass vessels of very large size by purely mechanical means has, however, been devised by P. Sievert. By the methods of this inventor glass vessels of quite unprecedented size—such as bath-tubs freely accommodating full grown men—can be produced. For this purpose the glass is spread out on the surface of a large cast-iron plate, provided with numerous small holes through which steam or compressed air may be blown when desired. The slab of viscous glass, when properly spread over this

plate, is clamped down against it all around the outside edge by means of a suitably shaped iron collar, which holds the glass in air-tight contact against the plate beneath. The whole iron plate, with the slab of glass clamped to it, is now turned over, so that the glass hangs down under the plate. The glass immediately begins to sag under its own weight, and is assisted in this tendency by a suitable blowing of steam or air into the space between the plate and the glass. In blowing bath tubs in this way the glass is allowed to distend downwards until the desired depth is attained, when further distension is arrested by bringing a flat supporting plate under the glass, which is pressed against this flat plate by the pressure of the air, thus forming the flat bottom of the tub. In this process the outline of the object is determined by the shape of the clamping bars or plate that fix the edges of the hot glass against the iron plate described above, and by this means almost any desired shape can be given to objects of simple form.

It is obvious that this process can also be employed for blowing a hollow body into contact with a mould of any desired form and forcing the hot glass to take the exact shape of the mould; for smaller bodies, however, the blowing in of separately generated steam is not required, the heat of the molten glass itself being used to generate the necessary steam. For this purpose the requisite quantity of glass is dropped on the surface of a wet slab of asbestos. On this surface the glass remains floating upon a layer of steam, which is constantly renewed by the intense heating action of the hot glass on the water contained in the asbestos below. The moulds used in this process are provided with a sharp edge or lip, and as soon as the glass has spread into a slab of sufficient size, the inverted mould is brought down upon the glass and pressed against it. The sharp lip or edge of the mould forces the glass into close contact with the asbestos under it all around the edge of the mould, thereby enclosing the space existing between the rest of the glass and the wet asbestos. The heat of the glass continues to generate steam at a rapid rate, but now the steam can no longer escape from under

the glass around the edges, and therefore blows the glass upwards into the mould, ultimately forcing it into intimate contact with the surface of the mould; when this is accomplished the pressure of the steam rises rapidly, and ultimately lifts the entire mould and glass sufficiently to allow the excess steam to escape—and this is the sign that the blowing is complete. The whole process takes only a very few seconds, and is very successful when applied to suitable glass and used with moulds of proper shape. It is, of course, obvious that ordinary narrow-mouthed bottles could not be produced in this way, but wide-mouthed bottles and jars are made in this manner, although the chief utility of the process lies in the production of comparatively shallow articles, which are not of a shape that lends itself to pressing.

CHAPTER IX

BLOWN AND PRESSED GLASS

In many ways very similar to the processes employed in the production of bottles are those used in the manufacture of all hollow glass vessels that are produced by blowing, either with or without the aid of moulds. Apart from the actual shapes of the articles themselves, however, the principal difference between bottles and the better classes of hollow glass ware lies in the composition and quality of the glass itself. In this respect all grades of manufacture are to be met with, from the light coloured greenish or bluish glass used for medicine bottles to the most perfectly colourless and brilliant "crystal" or flint glass. This gradation in the perfection of the glass represents a corresponding gradation in the care bestowed upon the choice of raw materials and the various manipulations of melting the glass. As we have seen, for the commonest kinds of bottles, where colour and quality are immaterial, all kinds of fusible materials can be utilised, loamy or ferruginous sands and refuse-glass of all kinds being employed. Where somewhat higher requirements have to be met, rather purer sands have to be used as sources of silica, while lime and alkali must be introduced in purer forms, the alkali in the shape of the cheapest qualities of salt-cake and the lime in that of lime-stones reasonably free from iron and magnesia. Finally, for the best qualities of glass the purest sand obtainable is used, being often specially washed to remove all loamy matter, while the alkali is introduced in the form of carbonate, a chemical product which in its better qualities is practically free from injurious impurities. In these high class products two very distinct kinds of glass are met with. One class, of which the Bohemian "crystal"

is a typical example, is chemically of the nature of an alkali-lime silicate, the alkali in the case of the Bohemian glass being potash; the other variety of glass contains no lime, its place being taken by lead, typical of this class being English flint glass. In some varieties of glass, lead is also replaced, partially or entirely, by barium, but this material is chiefly used for the manufacture of pressed glass.

The higher grades of quality in glass, which thus require increased refinement in the raw materials, also demand increased refinement in the furnaces and appliances employed in their melting. The tank-furnace, which holds the field in bottle-manufacture, is not so frequently met with in the production of the better qualities of glass-ware. In England the best grades of hollow glass-ware are inseparably associated with the highest quality of flint glass, which has hitherto been produced almost exclusively in covered pots, owing to the necessity of protecting the glass from all sources of possible contamination and from the reducing action of the furnace gases. Special types of pot-furnace have, however, been devised in which the presence of reducing gases near the surface of the glass in the pots is so well guarded against that even flint glass can be successfully melted in open pots. In the case of soda-lime or potash-lime glasses, such as those of Bohemia, however, no reducing gases need be feared and there is a strong tendency to introduce tank-furnaces for this purpose. The quantity required, however, is rarely sufficient to keep a large continuous tank at work, and efforts have therefore been made to evolve tank-furnaces suitable for much smaller outputs. A very small tank intended for continuous working would have the serious disadvantage that the glass would have neither space nor time to undergo fining—the melting and working ends of the tank would, in fact, be too close together. This has led to the evolution of the "day" tank, in which melting and fining goes on during the night, while towards morning the temperature is allowed to fall and the glass is "worked out" during the day, so that perhaps two-thirds of the contents of

the furnace are taken out, the tank being refilled during the next night.

In all processes for the production of hollow glass-ware the glass or "metal" is taken from the pot by the process of gathering which has already been described; where blown articles are to be produced, as distinct from pressed goods, the initial stage is always the formation of a small hollow globe or bulb at the end of the glass-blower's pipe. The subsequent manipulations depend upon the nature of the article to be produced. The article may either be made entirely by hand-work, or rather "chair" work, as it is usually called, or the manipulations may be facilitated and the product cheapened—while its character is, of course, also modified—by the aid of moulds, which are used to bring the object to its proper shape and to impress upon it certain decorative mouldings or markings. As we have already seen, ordinary bottles are now always blown with the aid of moulds, and frequently in machines, and the same applies to medicine bottles, lamp chimneys, and the bulbs for electric light; in connection with lamp-chimneys it should be noted that they are blown in moulds in the form of cylindrical bottles with a flat bottom and a domed top, the ends being subsequently cut off. Each "bottle" is frequently arranged so as to cut up into a pair of chimneys.

Many of the cheaper varieties of tumblers and glasses are also blown in moulds, but they can be, and sometimes are, produced by hand, and as their manufacture is typical of that of all hand-blown hollow ware, we shall now describe it in some detail as an example of this class of work.

The implements used by the glass-blower and his assistants for this work are few and simple. The largest item is the glass-blower's bench or chair, which is simply a rough wooden bench provided with two projecting side rails or arms. When finishing a piece of work the blower sits on this bench, and the pipe lies across the two rails in front of him in such a position that by rolling it backwards and forwards along the rails he can readily keep the pipe in gentle

rotation. In addition to the ordinary blower's pipe and a "pontil" or rod for attaching small quantities of glass whereby the piece in hand can be held, the only other tools used by the blower are a number of shears and pincers of various shapes which serve for cutting off, pressing in, and distending the glass as required, a flat board and a stone or metal plate or "marver" being also used for the purpose of moulding the glass.

As already indicated, the first step in the production of such an object as a tumbler consists in gathering a suitable quantity of

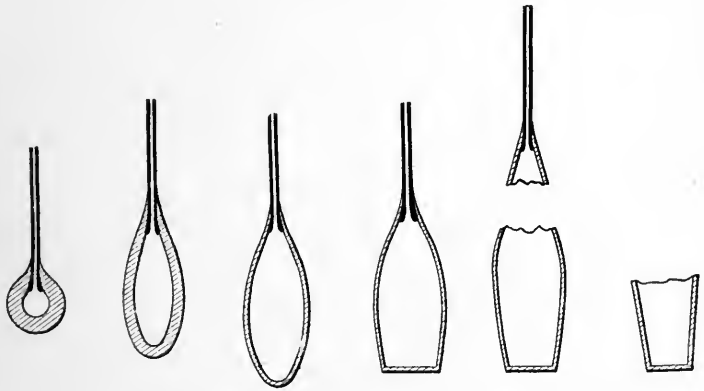

FIG. 10.—Sectional diagram of the evolution of a tumbler.

glass on the pipe and blowing it into a small bulb. This bulb is blown out to the proper size and is then elongated by gently swinging the pipe. The next step is the flattening of the lower end of the bulb by gently pressing it on the "marver" or flat plate provided for such purposes; in this way the flat bottom of the glass is formed, and the bulb now has the shape of the finished glass, but remains attached to the pipe by a shoulder and neck. The earliest practice was to separate the tumbler from the pipe at such a point as to leave the tumbler of the correct length, the remaining operation consisting in holding the glass, first fixed to a pontil for the purpose, into the furnace so as to heat the broken edge; this edge was thereby rounded off, and the brim of the glass could be widened or

otherwise shaped by rotating the glass or pressing it in or out by the aid of pieces of wood. In modern practice, however, this is not usual, the glass being separated from the pipe well above the shoulder and annealed in this shape. Subsequently the glass is finished in a trimming room or workshop by being cut off at the desired point and having the rough edge rounded off by the aid of a blowpipe flame. The cutting off operation is carried out in a great variety of ways, the most usual being by the action of heat applied locally and suddenly, either by the aid of specially shaped flat blowpipe flames or by an electrically heated wire. Machines for carrying out this operation, as well as the subsequent rounding of the edge automatically, are in use, but the latter process is sometimes replaced by slightly grinding and polishing the edges.

The evolution of an ordinary tumbler, as just described, and as illustrated diagrammatically in Fig. 10, is typical of the whole process of hollow-glass blowing, but of course the number of operations, as well as the care and skill involved in each step, increases rapidly as the form of the vessel becomes more complex; in the highest class of work a very considerable element of artistic taste and judgment on the part of the operative also becomes essential, for, although the form of the object as well as the colour and ornamentation are chosen by the designer, the blower has to translate the drawing of the designer into glass, and although his skill enables him to attain a considerable degree of fidelity in his rendering, many details remain at his own option, and the proper management of these is no small factor in the success of the whole work. The brief description given above applies to the method of production of all simple articles such as a tumbler, which can be blown out of a single mass of glass. In many cases more complex shapes are required, which are better produced by uniting several separate pieces. A typical example of this kind is furnished by an ordinary wine glass, in which the bowl and the stem are produced separately and put together while the glass is still hot enough to unite completely. The ordinary clear glass water jugs offer another example,

the thick handles being made separately and attached in a similar manner. In all such cases the necessity for building up the finished article out of several separate pieces arises from the fact that a thin blown portion requires to be united with a thick, heavy portion, or at least with a solid portion. The union of two such different pieces, however, entails a special difficulty, arising from the unequal rates of cooling of the thick, solid portion and the thin, hollow parts. Such composite articles, unless very carefully annealed, are apt to crack near the junction of the thin and thick parts—a feature sometimes met with in the water jugs already mentioned.

In this connection mention should perhaps be made of the application of colour and other decorations to this kind of glass. A very considerable range of effects of this kind is now available to the glass-worker. In the first place the body of the glass used for the production of the articles in question may be coloured by the addition of suitable colouring materials to the molten glass or raw materials, as explained in Chapter XII., but this procedure has very obvious limitations; where the article is built up of glass from several gatherings—as, for example, is the case in an ordinary wine glass, where the bowl, leg and foot are each made of separate gatherings—it is possible to use glass of different colours for these different parts, and this is commonly done in the production of wine glasses having ruby or green bowls and white legs and feet. A further modification in the application of colour is obtainable by taking up two or more gatherings on the same pipe and superposing a large gathering of white glass on a smaller one of coloured glass; this is analogous to the process of "flashing" sheet glass, described in Chapter XI., and this process lends itself to a variety of manipulations resulting in the distribution of the coloured layer of glass in almost any desired manner over the object in hand. The principal objection to this process, however, lies in the fact that pots of molten glass of all the colours desired must be kept available to the blower at the same time, and this is not easily arranged for in any reasonably economical manner. For this reason, and also

because the manipulations are simpler, coloured glass intended for application to blown glass ware is generally used in the form of short rods previously prepared; these rods are suitably heated, and the coloured glass can then be applied to the article in hand at any desired place and in as small or large a quantity as required. If the two glasses thus brought into contact are properly related to one another as regards chemical composition and physical properties, they blend very readily and perfectly, and the result is quite as good as could be obtained by using the coloured glass in the molten condition.

Other decorations, such as gilding or other metallic lustres and also various kinds of iridescence, are produced upon the finished glass. Metallic lustres are obtained by placing upon the surface of the glass, and slightly fusing into it, a layer of particles of the actual metal. In some cases this is done by rolling the glass vessel, while still hot, in a mass of metallic foil of the kind desired, when a sufficient quantity readily adheres; in other cases the metal is applied in the form of a flux or glaze containing a large proportion of an easily reduced compound of the metal, and this is afterwards reduced to the metallic state by the action of heat, sometimes aided by that of smoke or other reducing gases. An iridescent surface is produced upon certain varieties of glass by the corrosive action of acid vapours; in fact, in localities where the atmosphere is tainted with sulphur fumes it is quite usual to see an iridescent lustre on the surface of ordinary window glass. There are, of course, numerous other means of decorating blown and other glass, such as cutting, engraving, etching, silvering, etc., but it would lie beyond the scope of the present volume to deal with these, since they are outside the field of actual glass manufacture.

In the production of hollow glass-ware by hand, the glass-blower avails himself to the full of the property so characteristic of glass of assuming a pasty or viscous condition when suitably heated; by raising or lowering the temperature of his material, the blower can at will render it stiffer or more fluid; by blowing he can distend

it, draw it out by the aid of gravity or centrifugal action, or he can mould it with the aid of rods and tongs of suitable shape, while at times he allows it to fall or festoon under its own weight while held aloft. With all these manipulations at his disposal, the skilful operative is able to work the glass to his will and to fashion objects of great variety and beauty, but it should be noted that objects produced by hand in this way will bear the mark of the processes employed in their production in the fact that they do not possess the extreme regularity of size and shape which are associated with machine-made articles; there is a certain natural variability in the exact shape of curves and festoons that is foreign to the products of mechanical processes. For some purposes this variability is a disadvantage, while to some minds it appears as a defect, and methods have been devised for facilitating the production of strictly uniform glass-ware by the use of moulds as an aid to the work of the glass-blower. While undoubtedly reducing the value and beauty of the ware from the purely artistic standpoint, these aids to hand-work have rendered possible an immense expansion of the entire industry, since, with the use of moulds, presentable glass-ware can be produced by hands far less skilled than those required for pure hand-work.

In the description given above of bottle-blowing by hand we have already seen an example of the use of moulds in aiding the blower to form his object to the desired size and shape. Much more complicated and decorative objects can, however, be produced by the use of moulds. Such objects as globes and shades for gas, oil and electric lamps, when of a light substance and suitable shape, are usually produced by blowing bulbs of glass into moulds, where they acquire the general shape as well as the detailed decorated surface configuration which they afterwards present. Here again the body remains a closed vessel, and is only opened and trimmed to the final shape at the end of the operation when all the blowing and moulding have been done. Articles blown in this way very frequently show "mould marks," since the contact of the hot glass

with the relatively cold surface of the mould results in a certain crinkling or roughening of the surface, much as in the process of rolling. This effect can be minimised by dressing the interior surfaces of the moulds with suitable greasy dressings, whose chief property should be that they do not stick to the hot glass and leave little or no residue when gradually burnt away in the mould; the proper care of the moulds and their maintenance is in fact the first essential to successful manufacture in this as well as in the pressed-glass industry. Even under the most favourable conditions, however, the surface of glass blown into moulds is not so good as that of hand-blown articles which have never come into contact with cold materials, and therefore retain undiminished the natural "fire polish" which glass possesses when allowed to cool freely from the molten state. An effort at producing a similar brilliance of surface on moulded and pressed articles is often made by exposing them, after they have attained their final form, to the heat of a furnace to such an extent as to soften the surfaces and allow the glass to re-solidify under the undisturbed influence of surface-tension much as it would do in solidifying freely in the first place. Unfortunately this process cannot be carried out without more or less softening the entire article, so that skilful manipulation is required to prevent serious deformation of the object, while a certain amount of rounding off in all sharp corners and angles cannot be avoided.

The air-pressure required to bring the whole of the surfaces of a large and possibly complicated piece of glass into contact with the surfaces of the mould is sometimes very considerable, and the lung-power of the blower is often insufficient for the purpose; in many works, therefore, compressed air is supplied, arrangements being employed whereby the operative can quickly connect the mouthpiece of his pipe with the air-main, while he can accurately control the pressure by means of a suitable valve. The Sievert process of moulding by the aid of steam pressure has already been described.

Although the evolution of the industry scarcely followed this path, it is not a large step to pass from a process in which air pressure is used to drive viscous glass into contact with a mould to a process in which the pressure of the air is replaced by the pressure of a suitably-shaped solid plunger, and this is essentially the widely-used process of glass pressing. In the first instance this mode of manufacture is obviously applicable to solid or flat and shallow articles which could not be conveniently evolved from the spherical bulb which stands as embryo of all blown glass; at first sight it would seem in fact as though the process must be limited to articles of such a shape that a plunger can readily enter and leave the concave portions. By the ingenious device, however, of pressing two halves of a closed or nearly closed vessel simultaneously in two adjacent moulds and then pressing the two halves together while still hot enough to unite, it has been made possible to produce by the press alone such objects as water-jugs, for example, into which a plunger could not possibly be introduced when finished. The process of pressing being a purely mechanical one and requiring little skilled labour, has placed upon the market a host of cheap and extremely useful articles, thus serving to widen very considerably the useful applications of glass. On the other hand, the process has been and is still used to some extent for the production of articles intended to imitate the products of other processes such as hand-blown and cut glass, with the result that a great deal of glass has been produced which cannot possibly be classed as beautiful and much of which can lay as little claim to utility.

The essential feature of the process of glass pressing consists, as already indicated, in forcing a layer of glass into contact with a mould by the pressure of a mechanically actuated plunger. For this purpose a suitable mould and plunger as well as a press for holding the former and actuating the latter are required. The moulds are generally made of a special quality of close-grained cast-iron, and they are kept trimmed and dressed in much the same manner as the moulds used for blowing (except that the latter are

sometimes made of wood). For the purpose of facilitating the removal of the finished article the moulds are generally made in several pieces which fit into one another and can be separated by means of hinges. A very important point about these moulds is that the various pieces should fit accurately into one another, since otherwise a minute "fin" of glass will be forced into every interstice, and the traces of these fins will always remain visible on the finished article; the very perfect fit required entirely to prevent the formation of such fins is, of course, scarcely attainable in practice except in the case of new moulds, so that the traces of fins are generally to be found on all pressed articles, and serve as a ready means of identifying these products when an attempt is made to imitate better classes of glass-ware by their means. The presses used in this process were formerly hand-actuated, and some such machines are still in use in England; they are, however, regarded as entirely obsolete in America, where they have been replaced by "one man" machines which require the attendance of only one skilled man—the gatherer. The advantages claimed for the old manual lever machines—that the operator could apply just the right amount of pressure to press the glass home without risk of causing it to overflow the mould or to produce an excessive pressure upon the mould—is met in the new power presses by devices which carefully regulate the quantity of glass admitted into the mould. It is found, too, that the length of time for which the plunger is allowed to remain in contact with the glass in the mould is of very great importance to the quality of the glass produced, and the modern automatic machines are provided with means for regulating this length of contact. In operating these machines the gatherer drops the molten glass into the parison mould and in doing so pulls a lever or trigger which sets the machine in motion. The first action is the movement of a knife which cuts off the glass from the thread attaching it to the gatherer's iron and at the same time delimits the amount of glass in the mould. The plunger of the press then descends, remains in contact with the glass for the

desired time and then rises. The mould then moves to another position or "station," where it is opened and the glass withdrawn from it. In the older machines only one mould was used, but in order to save the time entailed by waiting for this mould to be freed of its glass, modern machines work with two or three moulds which are operated in succession. This not only increases the output of the machine, but also allows the moulds to maintain a better temperature and permits of their being carefully cleaned.

The presses themselves necessarily consist of the guides, levers and operating cams required to produce the successive movements of the plunger and moulds. It is, however, extremely important that the various parts of the press should retain their exact relative position throughout the operations, so that a high degree of rigidity in the framework is essential. For this reason the earlier machines, in which the whole of the appliances were supported on a single column, have now been superseded by presses in which the plunger and moulds are supported between two columns. In the process of pressing it will be seen that the glass is forced into intimate contact with the relatively cold surfaces of mould and plunger, and while undergoing this treatment the glass must remain sufficiently plastic readily to adapt itself to the configuration of the mould. It is therefore not surprising to find that the pressing process can only be used successfully with glass of a kind specially adapted for it. Certain varieties of flint glass and some barium glasses are used for this purpose, but the greater quantity of pressed glass, particularly as produced on the Continent, is made of a lime-alkali silicate containing considerable quantities of both soda and potash and relatively little lime; while sufficiently resistant for most purposes, this glass is particularly soft and adaptable while in the viscous condition.

The deleterious effect produced upon glass surfaces when brought into contact with relatively cold metal has already been referred to above, and it only remains to add that this is the principal difficulty with which the glass-pressing process has to contend. It is

overcome to some extent by the re-heating or "fire polishing" process, to which reference has already been made in connection with glass blown into moulds. If this is applied to the outside of a pressed article, however, the outlines of the pattern tend to become rounded. This difficulty, in its turn, is sometimes overcome by the application of a relatively small amount of "cutting," *i.e.*, of grinding and polishing in order to give a superior finish to the pressed article. If this is carried far enough the result is a much superior, but also a considerably more expensive article. The interior of pressed articles, however, cannot as a rule be covered with such a pattern of ridges, grooves, spirals or lozenges as would allow of finishing in this manner. For purposes of utility the interior surfaces of most articles require to be as smooth as possible. Here, therefore, the application of fire polishing finds a very useful field, but the difficulty that the general softening of the article may lead to its distortion or collapse becomes important. One method of avoiding this risk consists in carrying out the surface heating of the interior of the articles by means of jets of flame under pressure while the glass is still in the mould. This has the disadvantage that it keeps the mould occupied for too long a time and also raises the temperature of the mould to an undesirable extent. An improved method of operation, therefore, consists in removing the pressed article from the mould and keeping the outside stiff enough to resist deformation by means of a series of small jets of cold air playing upon the outside surface while the flames used for fire polishing play upon the inside. The strains set up by such drastic proceedings must, of course, be subsequently removed by annealing.

CHAPTER X

ROLLED OR PLATE-GLASS

In the present chapter we propose to deal with all those processes of glass manufacture in which the first stage consists in converting the glass into a slab or plate by some process of rolling. We have already considered the general character of the rolling process, and have seen that, although hot, viscous glass lends itself readily to being rolled into sheets or slabs, these cannot be turned out with a smooth, flat surface. In practice the surface of rolled glass is always more or less dimmed by contact with the minute irregularities of table or roller, and larger irregularities of the surface arise from the buckling that occurs at a great many places in the sheet. These limitations govern the varieties of glass which can be produced by processes that involve rolling, and have led to the somewhat curious result that both the cheapest and roughest, as well as the best and most expensive kinds of flat glass, are produced by rolling processes. Ordinary rough "rolled plate," such as that used in the skylights of workshops and of railway stations, is the extreme on the one hand, while polished plate-glass represents the other end of the scale. The apparent paradox is, however, solved when it is noted that in the production of polished plate-glass the character of the surface of the glass as it leaves the rollers is of very minor importance, since it is entirely obliterated by the subsequent processes of grinding, smoothing, and polishing. Intermediate between the rough "rolled" and the "polished" plate-glass we have a variety of glasses in which the appearance of the rolled surface is hidden or disguised to a greater or lesser extent by the application of a pattern that is impressed upon the glass during the rolling process; thus

we have rolled plate having a ribbed or lozenge patterned surface, or the well known variety of "figured rolled" plate, sometimes known as "Muranese," whose elaborate and deeply imprinted patterns give a very brilliant effect.

Rolled plate-glass being practically the roughest and cheapest form of glazing, is principally employed where appearance is not considered, and its chief requirement is, therefore, cheapness, although both the colour and quality of the glass are of importance as affecting the quantity and character of the light which is admitted to the building where the glass is used. On the ground of cheapness it will be obvious from what we have said above (Chapter V.), that such glass can only be produced economically in large tank-furnaces, and these are universally used for this purpose. The requirements as regards freedom from enclosed foreign bodies of small size and of enclosed air bells are not very high in such glass, and, therefore, tanks of very simple form are generally used. No refinements for regulating the temperature of various parts of the furnace in order to ensure perfect fining of the glass are required, and the furnace generally consists simply of an oblong chamber or tank, at one end of which the raw materials are fed in, while the glass is withdrawn by means of ladles from one or two suitable apertures at the other end. For economical working, however, the furnace must be capable of working at a high temperature, because a cheap glass mixture is necessarily somewhat infusible, at all events where colour is considered. This will be obvious if we remember that the fusibility of a glass depends upon its alkali contents, and alkali is the most expensive constituent of such glasses.

The actual raw materials used in the production of rolled plate-glass are sand, limestone and salt cake, with the requisite addition of carbon and of fluxing and purifying materials. The selection of these materials is made with a view to the greatest purity and constancy of composition which is available within the strictly set limits of price which the low value of the finished product entails. These materials are handled in very large quantities, outputs of

from 60 to 150 tons of finished glass per week from a single furnace being by no means uncommon; mechanical means of handling the raw materials and of charging them into the furnace are therefore adopted wherever possible.

The glass is withdrawn from the furnace by means of large iron ladles. These ladles are used of varying sizes in such a way as to contain the proper amount of glass for rolling into the various sizes of sheets required. The sizes used are sometimes very large, and ladles holding as much as 180 to 200 lbs. of glass are used. These ladles, when filled with glass, are not carried by hand, but are suspended from slings attached to trolleys that run on an overhead rail. The ladler, whose body is protected by a felt apron and his face by a mask having view holes glazed with green glass, takes the empty ladle from a water trough, in which it has been cooled, carries it to the slightly inclined gangway that leads up to the opening in the front of the furnace, and there introduces the ladle into the molten glass, giving it a half turn so as to fill it with a "solid" mass of glass. By giving the ladle two or three rapid upward jerks, the operator then detaches the glass in the ladle as far as possible from the sheets and threads of glass which would otherwise follow its withdrawal; then the part of the handle of the ladle near the bowl is placed in the hook attached to the overhead trolley, and by bearing his weight on the other end of the handle the workman draws the whole ladle up from the molten bath in the furnace and out through the working aperture. This operation only takes a few seconds to perform, but during this time the ladler is exposed to great heat, as a more or less intense flame generally issues from the working aperture, whence it is drawn upward under the hood of the furnace. Considerable advances have recently been made in protecting ladlers and others working close to furnaces at high temperatures from the inconveniences and dangers attending such work. The devices adopted include the use of a screen made of loose hanging chains suspended before the furnace opening. Unlike the solid furnace door, this

screen need not be removed when the ladle is being used, as the chains part readily to let the ladle pass and at the same time the interstices of the links allow the worker to obtain an adequate view of the interior of the furnace. Another useful device consists in the provision of a screen of cold air which is forced out under pressure just in front of the furnace opening; this cold air screen not only keeps the flame itself entirely away from the operator, but also cools the whole vicinity of the furnace in which he has to work. Its chilling effect on the contents of the ladle as it passes rapidly through the screen is negligible. Finally, the eyes of ladlers, and still more of gatherers and blowers, who are obliged to watch the molten glass for long periods of time, appear to require very special protection in order to avoid the risk of the eye disease known as "glass blowers' cataract." This disease has received much study, and the view is now held that it is due to the prolonged action of the invisible radiations (infra red and ultra violet, but principally the infra red) which molten glass sends out in very large quantities. Protection from these is best obtained by the wearing of spectacles made of special glasses which absorb these injurious rays while transmitting the necessary amount of light. Glasses for this purpose, in which some of the rare earth elements, notably cerium, are incorporated, have been developed as the result of a research by Sir William Crookes, and these promise to be of immense value to the glass workers.

From the furnace opening the ladler, generally aided by a boy, runs the full ladle to the rolling table and there empties the ladle upon the table just in front of the roller. In doing this, two distinctly different methods are employed. In one, only the perfectly fluid portion of the glass is poured out of the ladle by gradually tilting it, the chilled glass next to the walls of the ladle being retained there and ultimately returned to the furnace while still hot. In the other method the chilling of the glass is minimised as far as possible, and the entire contents of the ladle are emptied upon the rolling table by the ladler, who turns the entire ladle over with a

rapid jerk which is so arranged as to throw the coldest part of the glass well away from the rest. When the sheet is subsequently rolled this chilled portion is readily recognised by its darker colour, and since it lies entirely at one end of the sheet it is detached before the sheet goes any further. Neither method appears to present any preponderating advantage.

The rolling table used in the manufacture of rolled plate is essentially a cast-iron slab of sufficient size to accommodate the largest sheet which is to be rolled; over this slab moves a massive iron

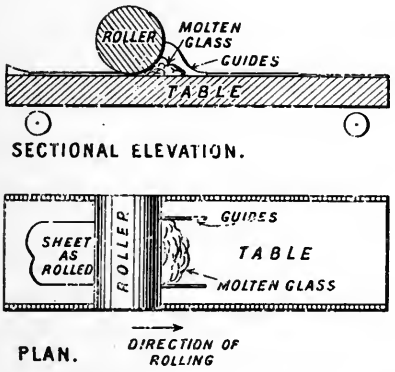

FIG. 11.—Rolling table for rolled plate-glass.

roller which may be actuated either by hand or by mechanical power—the latter, however, being now almost universal. The thickness of the sheet to be rolled is regulated by means of slips of iron placed at the sides of the table in such a way as to prevent the roller from descending any further towards the surface of the table: so long as the layer of glass is thicker than these slips, the entire weight of the roller comes upon the soft glass and presses it down, but as soon as the required thickness is attained the weight of the roller is taken by the iron slips and the glass is not further reduced in thickness. The width of the sheet is regulated by means of a pair of iron guides, formed to fit the forward face of the roller and the surface of the table, in the manner indicated in Fig. 11.

The roller, as it moves forward, pushes these guides before it, and the glass is confined between them. When the roller has passed over the glass, the sheet is left on the iron table in a red-hot, soft condition, and it must be allowed to cool and harden to a certain extent before it can be safely moved. In this interval the chilled portion—if any—is partially severed by an incision made in the sheet by means of a long iron implement somewhat like a large knife, and then the sheet is loosened from the bed of the table by passing under it, with a smooth, rapid stroke, a flat bladed iron tool. The sheet is next removed to the annealing kiln or "lear," being first drawn on to a stone slab and thence pushed into the mouth of the kiln. At this stage the chilled portion of the sheet is completely severed by a blow which causes the glass to break along the incision previously made.

The rolled plate annealing kiln is essentially a long, low tunnel, kept hot at one end, where the freshly rolled sheets are introduced, and cold at the other end, the temperature decreasing uniformly down the length of the tunnel. The sheets pass down this tunnel at a slow rate, and are thus gradually cooled and annealed sufficiently to undergo the necessary operations of cutting, etc. Although thus simple in principle, the proper design and working of these "lears" is by no means simple or easy, since success depends upon the correct adjustment of temperatures throughout the length of the tunnel and a proper rate of movement of the sheets, while the manner of handling and supporting the sheets is vital to their remaining flat and unbroken. The actual movement of the sheets is effected by a system of moving grids which run longitudinally down the tunnel. The sheets ordinarily lie flat upon the stone slabs that form the floor of the tunnel, and the grids are lowered into recesses cut to receive them. At regular intervals of time the iron grid bars are raised just sufficiently to lift the sheets from the bed of the kiln, and are then moved longitudinally a short distance carrying the sheets forward with them and immediately afterwards again depositing them on the stone bed. The grids return to their

former position while lowered into their recesses below the level of the kiln bed.

When they emerge from the annealing kiln or "lear" the sheets of rolled plate-glass are carried to the cutting and sorting room. Here the sheets are trimmed and cut to size. The edges of the sheets as they leave the rolling table are somewhat irregular, and sometimes a little "beaded," while the ends are always very irregular. Ends and edges are therefore cut square or "trimmed" by the aid of the cutting diamond. For this purpose the sheet is laid upon a flat table, the smoothest side of the sheet being placed upwards, and long cuts are taken with a diamond—good diamonds of adequate size and skilful operators being necessary to ensure good cutting on such thick glass over long lengths. Strips of glass six or eight feet long and half an inch wide are frequently detached in the course of this operation, and the final separation is aided by slight tapping of the underside of the glass just below the cut and—if necessary—by breaking the strip off with the aid of suitable tongs.

No very elaborate "sorting" of rolled plate-glass is required, except perhaps that the shade of colour in the glass may vary slightly from time to time, and it is generally preferable to keep to one shade of glass in filling any particular order. Apart from this, the rolled plate cutter has merely to cut out gross defects which would interfere too seriously with the usefulness of the glass. As we have already indicated, air bells and minute enclosures of opaque matter are not objectionable in this kind of glass, but large pieces of opaque material must generally be cut out and rejected, not only because they are too unsightly to pass even for rough glazing purposes, but also because they entail a considerable risk of spontaneous cracking of the glass—in fact, visible cracks are nearly always seen around large "stones," as these inclusions are called. These may arise from various causes, such as incomplete melting of the raw materials, or the contamination of the raw materials with infusible impurities, but the most fruitful source of trouble in this direction lies in the crumbling of the furnace

lining, which introduces small lumps of partially melted fire-clay into the glass. In a rolled plate tank-furnace which is properly constructed and worked, the percentage of sheets which have to be cut up on account of such enclosures should be very small, at all events until the furnace is old, when the linings naturally show an increasing tendency to disintegrate.

Returning now to the rolling process, it is readily seen that a very slight modification will result in the production of rolled plate-glass having a pattern impressed upon one surface; this

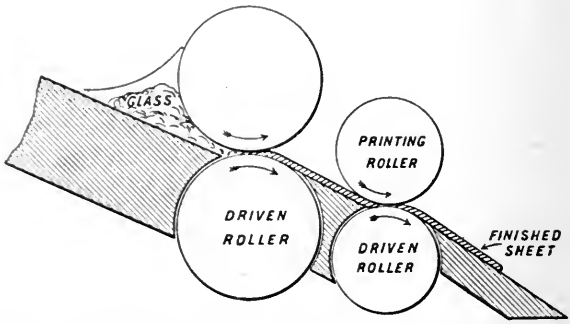

FIG. 12.—Sectional diagram of machine for rolling "figured rolled" plate-glass.

modification consists in engraving upon the cast iron plate of the rolling table in intaglio any pattern that is to appear upon the glass in relief. As a matter of fact only very simple patterns are produced in this way, such as close parallel longitudinal ribbing and a lozenge pattern, the reason probably being that the cost of cutting an elaborate pattern over the large area of the bed plate of one of these tables would be very considerable. Further, as these tables and their bed plates are so very heavy, they are not readily interchanged or left standing idle, so that only patterns required in very great quantity could be profitably produced in this way. These disadvantages are, however, largely overcome by the double-rolling machine. In this machine, into whose rather elaborate

details we cannot enter here, the glass is rolled out into a sheet of the desired size and thickness by being passed between two rollers revolving about stationary axes, the finished sheet emerging over another roller, and passing on to a stone slab that moves forward at the same rate as the sheet is fed down upon it. In this machine a pattern can be readily imprinted upon the soft sheet as it passes over the last roller by means of a fourth roller, upon which the pattern is engraved; this is pressed down upon the sheet, and leaves upon it a clear, sharp and deep impress of its pattern. The general arrangement of the rollers in this machine is shown in the diagram of Fig. 12, which represents the sectional elevation of the appliance. After leaving the rolling machine, the course of the "figured rolled plate" produced in this manner is exactly similar to that of ordinary rolled plate, except that as a somewhat softer kind of glass is generally used for "figured," the temperature of the annealing kilns requires somewhat different adjustment. The cutting of the glass also requires rather more care, and it should be noted that such glass can only be cut with a diamond on the smooth side; the side upon which the pattern has been impressed in relief cannot be materially affected by a diamond. This is one reason why it is not feasible to produce such glass with a pattern on both sides.

Figured rolled glass, being essentially of an ornamental or decorative nature, is generally produced in either brilliantly white glass or in special tints and colours, and the mixtures used for attaining these are, of course, the trade property of the various manufacturers; the whiteness of the glass, however, is only obtainable by the use of very pure and, therefore, expensive materials. As regards the coloured plate-glasses, a general account of the principles underlying the production of coloured glass will be found in Chapter XII.

The manufacture of polished plate-glass really stands somewhat by itself, almost the only feature which it has in common with the branches of manufacture just described being the initial rolling process.

The raw materials for the production of plate-glass are chosen with the greatest possible care to ensure purity and regularity; owing to the very considerable thickness of glass which is sometimes employed in plate, and also to the linear dimensions of the sheets which allow of numerous internal reflections, the colour of the glass would become unpleasantly obtrusive if the shade were at all pronounced. The actual raw materials used vary somewhat from one works to another; but, as a rule, they consist of sand, limestone, and salt-cake, with some soda ash and the usual additions of fluxing and purifying material such as arsenic, manganese, etc. The glass is generally melted in pots, and extreme care is required to ensure perfect melting and fining, since very minute defects are readily visible in this glass when finished, and, of course, detract most seriously from its value.

The method of transferring the glass from the melting pot to the rolling table differs somewhat in different works. In many cases the melting pots themselves are taken bodily from the furnace and emptied upon the bed plate of the rolling machine, while in other cases the glass is first transferred to smaller "casting" pots, where it has to be heated again until it has freed itself from the bubbles enclosed during the transference, and then these smaller pots are used for pouring the glass upon the rolling slab. The advantage of the latter more complicated method lies, no doubt, in the fact that the large melting pots, which have to bear the brunt of the heat and chemical action during the early stages of melting, are not exposed to the great additional strain of being taken from the hot furnace and exposed for some time to the cold outside air. Apart from the mechanical risks of fracture, this treatment exposes the pots to grave risks of breakage from unequal expansion and contraction on account of the great differences of temperature involved. Where smaller special casting-pots are used these are not exposed to such prolonged heat in the furnace, and are never exposed to the chemical action of the raw materials, so that these subsidiary pots may perhaps be made of a material

better adapted to withstand sudden changes of temperature than the high-class fire-clay which must be used in the construction of melting pots. On the other hand, the transference of the glass from the melting to the casting pots involves a laborious operation of ladling and the refining of the glass, with its attendant expenditure of time and fuel. Finally, the production of plate-glass in tank-furnaces could only be attempted by the aid of such casting pots in which the glass would have to undergo a second fining after being ladled from the tank, and this would materially lessen the economy of the tank for this purpose, while it is by no means an easy matter to produce in tank-furnaces qualities of glass equal as regards colour and purity to the best products of the pot furnace.

The withdrawal of the pots containing the molten glass from the furnace is now universally carried out by powerful machinery. The pots are provided on their outer surface with projections by which they can be held in suitably shaped tongs or cradles. A part of the furnace wall, which is constructed each time in a temporary manner, is broken down ; the pot is raised from the bed or " siege " of the furnace by the aid of levers, and is then bodily lifted out by means of a powerful fork. The pot is then lifted and carried by means of cranes until it is in position above the rolling table ; there the pot is tilted and the glass poured out in a steady stream upon the table, care being taken to avoid the inclusion of air bells in the mass during the process of pouring. When empty the pot is returned to the furnace as rapidly as possible, the glass being meanwhile rolled out into a slab by the machine. Except for the greater size and weight of both table and roller, the plate-glass rolling table is similar to that already described in connection with rolled plate. Of course, since the glass is poured direct from the pot, there is no chilled glass to be removed. Further, owing to the large size of sheets frequently required, the bed of the rolling table cannot be made of a single slab of cast-iron, a number of carefully jointed plates being, in fact, preferable, as they are less liable to warp under the action of the hot glass.

In arranging the whole of the rolling plant, the chief consideration to be kept in mind is that it is necessary to produce a flat sheet of glass of as nearly as possible equal thickness all over. The final thickness of the whole slab when ground and polished into a sheet of plate glass must necessarily be slightly less than that of the thinnest part of the rough rolled sheet. If, therefore, there are any considerable variations of thickness, the result will be that in some parts of the sheet a considerable thickness of glass will have to be removed during the grinding process. This will arise to a still more

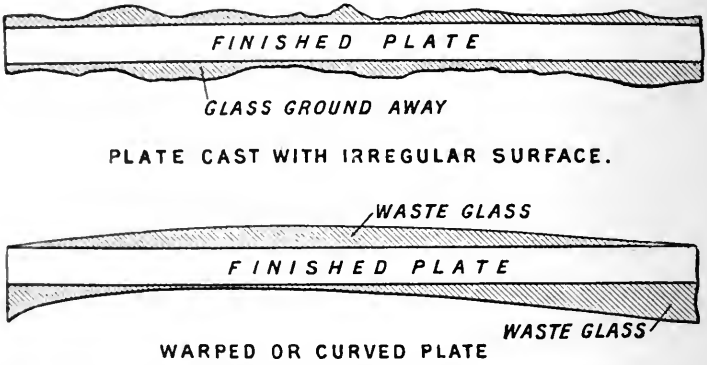

FIG 13.—Sectional diagram illustrating waste of glass in grinding curved or irregular plate.

serious extent if the sheet as a whole should be bent or warped so as to depart materially from flatness. The two cases are illustrated diagrammatically in Fig. 13, which shows sectional views of the sheets before and after grinding on an exaggerated scale.

While it is evident that careful design of the rolling table will avoid all tendency to the formation of sheets of such undesirable form, it is a much more difficult matter to avoid all distortion of the sheet during the annealing process and while the sheet is being moved from the rolling table to the annealing kiln. Owing to the great size of the slabs of glass to be dealt with, and still more to the stringent requirement of flatness, the continuous annealing kiln,

in which the glass travels slowly down a tunnel from the hot to the cold end, has not been adopted for the annealing of plate-glass, and a form of annealing kiln is still used for that glass which is similar in its mode of operation to the old-fashioned kilns that were used for other kinds of glass before the continuous kiln was introduced. These kilns simply consist of chambers in which the hot glass is sealed up and allowed to cool slowly and uniformly during a more or less protracted period. In the case of plate-glass the slabs are laid flat on the stone bed of the kiln. This stone bed is built up of carefully dressed stone, or blocks of fire-brick bedded in sand in such a way that they can expand freely laterally without causing any tendency for the floor to buckle upwards as it would do if the blocks were set firmly against one another. The whole chamber is previously heated to the requisite temperature at which the glass still shows a very slight plasticity. The hot glass slabs from the rolling table are laid upon the bed of this kiln, several being usually placed side by side in the one chamber, and the slabs in the course of the first few hours settle down to the contour of the bed of the kiln, from which shape and position they are never disturbed until they are removed when quite cold. In modern practice the cooling of a kiln is allowed to occupy from four to five days; even this rate of cooling is only permissible if care is taken to provide for the even cooling of all parts of the kiln, and for this purpose special air passages are built into the walls of the chamber and beneath the bed upon which the glass rests, and air circulation is admitted to these in such a way as to allow the whole of the kiln to cool down at the same rate; in the absence of such special arrangements, the upper parts of the kiln would probably cool much more rapidly than the base, so that the glass would be much warmer on its under than on its upper surface.

When the slabs of plate-glass are removed from the annealing kilns they very closely resemble sheets of rolled plate in appearance, and they are quite sufficiently transparent to allow of examination and the rejection of the more grossly defective portions; the more

minute defects, of course, can only be detected after the sheets have been polished, but this preliminary examination saves the laborious polishing of much useless glass.

The process of grinding and polishing plate-glass consists of three principal stages. In the first stage the surfaces of the glass are ground so as to be as perfectly flat and parallel as possible; in order to effect this object as rapidly as possible, a coarse abrasive is used which leaves the glass with a rough grey surface. In the second stage, that of smoothing, these rough grey surfaces are ground down with several grades of successively finer abrasive until finally an exceedingly smooth grey surface is left. In the third and final stage the smooth grey surface is converted into the brilliant polished surface with which we are familiar by the action of a polishing medium.

Originally the various stages of the grinding and polishing processes were carried out by hand, but a whole series of ingenious machines has been produced for effecting the same purpose more rapidly and more perfectly than hand labour could ever do. We cannot hope to give any detailed account of the various systems of grinding and polishing machines which are even now in use, but must content ourselves with a survey of some of the more important considerations governing the design and construction of such machinery.

In the first place, before vigorous mechanical work can be applied to the surface of a plate of glass, that plate must be firmly fixed in a definite position relatively to the rest of the machinery, and such firm fixing of a plate of glass is by no means readily attained, since the plate must be supported over its whole area if local fracture is to be avoided. While the surface of the plate is in the uneven condition in which it leaves the rolling table, such a firm setting of the glass can only be attained by bedding it in plaster, and this must be done in such a manner as to avoid the formation of air-bubbles between plaster and glass; if bubbles are allowed to form, they constitute places where the glass is unsupported. During the

grinding and polishing processes these unsupported places yield to the heavy pressure that comes upon them, and irregularities in the finished polished surfaces result. The most perfect adhesion between glass and plaster is attained by spreading the paste of plaster on the upturned surface of the slab of glass and lowering the iron bed plate of the grinding table down upon it, the bed plate with the adhering slab of glass being afterwards turned over and brought into position in the grinding machine. When one side of the glass has been polished it is generally found sufficient to lay the slab down on a bed of damp cloth, to which it adheres very firmly, although sliding is entirely prevented by a few blocks fixed to the table in such a way as to abut against the edges of the sheet. In many works, however, the glass is set in plaster for the grinding and polishing of the second side as well as of the first.

The process of grinding and polishing is still regarded in many plate-glass works as consisting of three distinct processes, known as rough grinding, smoothing and polishing respectively. Formerly these three stages of the process were carried out separately; at first by hand, and later by three different machines. In the most modern practice, however, the rough and smooth grinding are done on the same machine, the only change required being the substitution of a finer grade of abrasive at each step for the coarser grade used in the previous stage. For the polishing process, however, the rubbing implements themselves must be of a different kind, for while the grinding and smoothing is generally done by means of cast-iron rubbers moving over the glass, the polishing is done with felt pads. The table of the machine, to which the glass under treatment is attached, is therefore made movable, and when the grinding and smoothing processes are complete, the table with its attached glass is moved so as to come beneath a superstructure carrying the polishing rubbers, and the whole is then elevated so as to allow the rubbers to bear on the glass.

The earliest forms of grinding machines gave a reciprocal motion to the table which carries the glass, or the grinding rubbers were

moved backward and forward over the stationary table. Rotary machines, however, were introduced and rapidly asserted their superiority, until, at the present time, practically all plate-glass is ground on rotating tables, some of these attaining a diameter of over 30 ft. The grinding "rubbers" consist of heavy iron slabs, or of wood boxes shod with iron, but of much smaller diameter than the grinding table. The rubbers themselves are rotary, being caused to rotate either by the frictional drive of the rotating table below them, or by the action of independent driving mechanism, but the design of the motions must be so arranged that the relative motion of rubber and glass shall be approximately the same at all parts of the glass sheets, otherwise curved instead of plane surfaces would be formed. This condition can be met by placing the axes of the rubbers at suitable points on the diameter of the table. The abrasive is fed on to the glass in the form of a thin paste, and when each grade or "course" has done the work required of it, the whole table is washed down thoroughly with water and then the next finer grade is applied. The function of the first or coarsest grade is simply to remove the surface irregularities and to form a rough but plane surface. The abrasive ordinarily employed is sharp sand, but only comparatively light pressure can be applied, especially at the beginning of this stage, since at that period the weight of the rubber is at times borne by relatively small areas of glass that project here and there above the general level of the slab. As these are ground away, the rubbers take a larger and more uniform bearing, and greater pressure can be applied. The subsequent courses of finer abrasives are only required to remove the coarse pittings left in the surface by the action of the first rough grinding sand; the finer abrasive replaces the deep pits of the former grade by shallower pits, and this is carried on in a number of steps until a very smooth "grey" surface is attained and the smoothing process is complete. The revolving table or "platform" is now detached from the driving mechanism, and moved along suitably placed rails on wheels provided for that purpose, until it

stands below the polishing machine. Here it is attached to a fresh driving mechanism, and it is then either raised so as to bring the glass into contact with the felt-covered polishing rubbers, or the latter are lowered down upon the glass. The polishing rubbers are large felt-covered slabs of wood or iron which are pressed against the glass with considerable force; their movement is very similar to that of the grinding rubbers, but in place of an abrasive they are supplied with a thin paste of rouge and water. The time required for the polishing process depends upon the perfection of the smoothing that has been attained; in favourable cases two or three hours are sufficient to convert the "grey" surface into a perfectly polished one; where, however, somewhat deeper pits have been left in the glass, the time required for polishing may be much longer, and the polish attained will not be so perfect. The mode of action of a polishing medium such as rouge is now recognised to be totally different in character from that of even the finest abrasive; the grains of the abrasive act by their hardness and the sharpness of their edges, chipping away tiny particles of the glass, so that the glass steadily loses weight during the grinding and smoothing processes. During the polishing process, however, there is very little further loss of weight, the glass forming the hills or highest parts of the minutely pitted surface being dragged or smeared over the surface in such a way as gradually to fill up the pits and hollows. The action of the polishing medium is probably partly chemical and partly physical, but it results, together with the pressure of the rubber, in giving to the surface molecules of the glass a certain amount of freedom of movement, similar to that of the molecules of a viscid liquid; the surface layers of glass are thus enabled to "flow" under the action of the polisher and to smooth out the surface to the beautiful level smoothness which is so characteristic of the surfaces of liquids at rest. This explanation of the polishing process enables us to understand why the proper consistency of the polishing paste, as well as the proper adjustment of the speed and pressure of the rubbers, plays such an important part in successful

polishing; it also serves to explain the well-known fact that rapid polishing only takes place when the glass surface has begun to be perceptibly heated by the friction spent upon it.

It has been estimated that, on the average, slabs of plate-glass lose one-third of their original weight in the grinding and polishing processes, and it is obvious that the erosion of this great weight of glass must absorb a large amount of mechanical energy, while the cost of the plant and upkeep is proportionately great. Every factor that tends to diminish either the total weight of glass to be removed per square yard of finished plate, or reduces the cost of removal, must be of the utmost importance in this manufacture. The flatness of the plates as they leave the annealing kiln has already been referred to, and the reason why the processes of grinding and polishing have formed the subject for innumerable patents will now be apparent. The very large expansion of the use of plate-glass in modern building construction, together with the steady reduction in the prices of plate, are evidence of the success that has attended the efforts of inventors and manufacturers in this direction.

At the present time plate-glass is manufactured in very large sheets, measuring up to 26 ft. in length by 14 ft. in width, and in thickness varying from $\frac{3}{16}$th of an inch up to $1\frac{1}{2}$ in., or more, for special purposes. At the same time the quality of the glass is far higher to-day than it was at earlier times. This high quality chiefly results from more careful choice of raw materials and greater freedom from the defects arising during the melting and refining processes, while rigid inspection is applied to the glass as it comes from the polishing machines. For this purpose the sheets are examined in a darkened room by the aid of a lamp placed in such a way that ts oblique rays reveal every minute imperfection of the glass; these imperfections are marked with chalk, and the plate is subsequently cut up so as to avoid the defects that have thus been detected.

Perhaps the most remarkable fact about the quality of modern plate-glass is its relatively high degree of homogeneity. Glass, as

we have seen in Chapter I., is not a chemically homogeneous substance, but rather a mixture of a number of substances of different density and viscosity. Wherever this mixture is not sufficiently intimate, the presence of diverse constituents becomes apparent in the form of striæ, arising from the refraction or bending of light-rays as they pass from one medium into another of different density. Except in glass that has undergone elaborate stirring processes, such striæ are never absent, but the skill of the glass-maker consists in making them as few and as minute as possible, and causing them to assume directions and positions in which they shall be as inconspicuous as possible. In plate-glass this is generally secured in a very perfect manner, and to ordinary observation no striæ are visible when a piece of plate glass is looked at in the ordinary way, *i.e.*, through its smallest thickness; if the same piece of glass be looked at transversely, the edges having first been polished in such a way as to render this possible, the glass will be seen to be full of striæ, generally running in fine lines parallel with the polished surfaces of the glass. This uniform direction of the striæ is partly derived from the fact that the glass has been caused to flow in this direction by the action of the roller when first formed into a slab, but this process would not obliterate any serious inequalities of density which might exist in the glass as it leaves the pot, so that successful results are only attainable if great care is taken to secure the greatest possible homogeneity in the glass during the melting process.

At the present time probably the greater bulk of plate-glass is used for the purpose of glazing windows of various kinds, principally the show windows of shops, etc. As used for this purpose the glass is finished when polished and cut to size. The only further manipulation that is sometimes required is that of bending the glass to some desired curvature, examples of bent plate-glass window panes being very frequently seen. This bending is carried out on the finished glass, *i.e.*, after it has been polished; the glass is carefully heated in a special furnace until softened, and is then gently made to lie against a stone or metal mould which has been provided with

the desired curvature. It is obvious that during this operation there are great risks of spoiling the glass; roughening of the surface by contact with irregular surfaces on either the mould, the floor of the kiln, or the implements used in handling the glass, can only be avoided by the exercise of much skill and care, while all dust must also be excluded since any particles settling on the surface of the hot glass would be "burnt in," and could not afterwards be detached. Small defects can, of course, be subsequently removed by local hand polishing, and this operation is nearly always resorted to where polished glass has to undergo fire treatment for the purpose of bending.

In addition to its use for glazing in the ordinary sense, plate-glass is employed for a number of purposes; the most important and frequent of these is in the construction of the better varieties of mirrors. For this purpose the glass is frequently bevelled at the edges, and sometimes a certain amount of cutting is also introduced on the face of the mirror. Bevelling is carried out on special grinding and polishing machines, and a great variety of these are in use at the present time. The process consists in grinding off the corners of the sheet of glass and replacing the rough perpendicular edge left by the cutting diamond by a smooth polished slope running down from the front surface to the lower edge at an angle of from 45 to 60 degrees. Since only relatively small quantities of glass have to be removed, small grinding rubbers only are used, and in some of the latest machines these take the form of rapidly-revolving emery or carborundum wheels. These grinding wheels have proved so successful in grinding even the hardest metals that it is surprising to find their use in the glass industry almost entirely restricted to the "cutting" of the better kinds of flint and "crystal" glass for table ware or other ornamental purposes. The reason probably lies in the fact that the use of such grinding wheels results in the generation of a very considerable amount of local heat, this effect being intensified on account of the low heat-conducting power of glass. If a piece of glass be held even lightly against a rapidly-

revolving emery wheel it will be seen that the part in contact with the wheel is visibly red-hot. This local heating is liable to lead to chipping and cracking of the glass, and these are the troubles actually experienced when emery or carborundum grinding is attempted on larger pieces of glass. In the case of at least one modern bevel-grinding machine, however, it is claimed that the injurious effects of local heating are avoided by carrying out the entire operation under water.

For the purpose of use in mirrors, plate-glass is frequently silvered, and this process is carried on so extensively that it has come to constitute an entire industry which has no essential connection with glass manufacture itself; for that reason we do not propose to enter on the subject here, only adding that the nature and quality of the glass itself considerably affects the ease and success of the various silvering processes. Ordinary plate-glass, of course, takes the various silvering coatings very easily and uniformly, but there are numerous kinds of glass to which this does not apply, although there are probably few varieties of glass which are sufficiently stable for practical use, and to which a silvering coating cannot be satisfactorily applied, provided that the most suitable process be chosen in each case.

While there is little, if any, use for coloured glass in the form of polished plate, entirely opaque plate-glass, coloured both black and white, is used for certain purposes. Thus, glass fascias over shop-fronts, the counters and shelves of some shops, and even tombstones are sometimes made of black or white polished plate. From the point of view of glass manufacture, however, these varieties only differ from ordinary plate-glass in respect of certain additions to the raw materials, resulting in the production of the white or black opacity. The subsequent treatment of the glass is identical with that of ordinary plate-glass, except that these opaque varieties are rarely required to be polished on both sides, so that the operations are simplified to that extent.

Certain limitations to the use of all kinds of plate-glass, whether

rough-rolled, figured or polished, were formerly set by the fact that under the influence of fire, partitions of glass were liable to crack, splinter and fall to pieces, thus causing damage beyond their own destruction and leaving a free passage for the propagation of the fire. To overcome these disadvantages, glass manufacturers have been led to introduce a network or meshing of wire into the body of such glass. Provided that the glass and wire can be made so as to unite properly, then the properties of such reinforced or "wired" glass should be extremely valuable. In the event of breakage from any cause, such as fire or a violent blow, while the glass would still crack, the fragments would be held together by the wire network, and the plates of glass as a whole would remain in place, neither causing destruction through flying fragments nor allowing fire or, for the matter of that, burglars a free passage. The utility of such a material has been readily recognised, but the difficulty lies in its production. These difficulties arise from two causes. The most serious is the considerable difference between the thermal expansion of the glass and of the wire to be embedded in it. The wire is necessarily introduced into red-hot glass while the latter is being rolled or cast, and therefore glass and wire have to cool down from a red heat together. During this cooling process the wire contracts much more than the glass, and breakage either results immediately, or the glass is left in a condition of severe strain and is liable to crack spontaneously afterwards. An attempt has been made to overcome this difficulty by using wire made of a nickel steel alloy, whose thermal expansion is very similar to that of glass; but, as a matter of fact, this similarity of thermal expansion is only known to hold for a short range of moderate temperatures, and probably does not hold when the steel alloy is heated to redness. In another direction, greater success is to be attained by the use of wire of a very ductile metal which should yield to the stress that comes upon it during cooling; probably copper wire would answer the purpose, but the great cost of copper is a deterrent from its use. A second difficulty is met with in intro-

ducing wire netting into glass during the rolling operation, and this lies in effecting a clean join between glass and wire. Most metals when heated give off a considerable quantity of gas, and when this gas is evolved after the wire has been embedded in glass, numerous bubbles are formed, and these not only render the glass very unsightly but also lessen the adhesion between the wire and the glass. This difficulty, however, can be overcome more readily than the first, since the surface of the metal can be kept clean and the gas expelled from the interior of the wire by preliminary heating. In spite of these difficulties, however, wired plate-glass is now successfully manufactured and has attained a definite commercial importance.

CHAPTER XI

SHEET AND CROWN GLASS

In the preceding chapter we have dealt with the processes of manufacture employed in the production of both the crudest and the most perfect forms of flat glass as used for such purposes as the glazing of window openings. The products now to be dealt with are of an intermediate character, sheet-glass possessing many of the properties of polished plate, but lacking some very important ones; thus sheet-glass is sufficiently transparent to allow an observer to see through it with little or no disturbance—in the best varieties of sheet-glass the optical distortion caused by its irregularities is so small that the glass appears nearly as perfect as polished plate—but in the cheap glass that is used for the glazing of ordinary windows, sheets are often employed which produce the most disturbing and sometimes the most ludicrous, distortions of objects seen through them. It is a curious fact that even in good houses the use of such inferior glass is tolerated without comment, the general public being, apparently, remarkably non-observant in this respect. In another direction sheet-glass has the great advantage over plate-glass that it is very much lighter, or can at least be produced of much smaller weight and thickness, although this advantage entails the consequent disadvantage that sheet-glass is usually much weaker than plate, and can only be used in much smaller sizes. In recent times the production of relatively thin plate-glass has, however, made such strides that it is now possible to obtain polished plate-glass thin enough and light enough for almost every architectural purpose. Finally, the most important advantage of sheet-glass, and the one which alone secures its use in a great number of

cases in preference to plate-glass, is its cheapness, the price of ordinary sheet-glass being about one-fourth that of plate-glass of the same size.

The raw materials for the manufacture of sheet-glass are sand, limestone, salt-cake, and a few accessory substances, such as arsenic, oxide of manganese, anthracite coal or coke, which differ considerably according to the practice of each particular works. In a general way these materials have already been dealt with in Chapter III., and we need only add here that the sheet-glass manufacturer must keep in view two decidedly conflicting considerations. On the one hand the requirements made in the case of sheet-glass as regards colour and purity render a rigorous choice of raw material and the exclusion of anything at all doubtful very desirable; but on the other hand the chief commercial consideration in connection with this product is its cheapness, and in order to maintain a low selling price at a profit to himself the manufacturer must rigorously exclude all expensive raw materials. For this reason sheet-glass works such as those of Belgium and some parts of Germany, which have large deposits of pure sand close at hand, possess a very considerable advantage over those in less favoured situations, since sand in particular forms so large a proportion of the glass, and the cost of carriage frequently exceeds, and in many cases very greatly exceeds, the actual price of the sand itself. The same considerations will apply, although in somewhat lesser degree, to the other bulky materials, such as limestone and salt-cake; but both these are more generally obtainable at moderate prices than are glass-making sands of adequate quality for sheet manufacture.

Ordinary " white " sheet-glass is now almost universally produced in tank-furnaces, and a very great variety of these furnaces are used or advocated for the purpose. It would be beyond the scope of the present book to enter in detail into the construction of these various types of furnace or to discuss their relative merits at length. Only a brief outline of the chief characteristics of the most important forms of sheet tank-furnaces will therefore be given here.

Sheet tanks differ from each other in several important respects; these relate to the sub-division of the tank into one, two, or even three more or less separate chambers, to the depth of the bath of molten glass and the height of the "crown" or vault of the furnace chamber, to the shape and position of the apertures by which the gas and air are admitted into the furnace, and the resultant shape and disposition of the flame, and finally to the position and arrangement of the regenerative appliances by which some of the heat of the waste gases is returned into the furnace.

Taking these principal points in order, we find that in some sheet tank-furnaces the whole furnace constitutes a single large chamber. In this type of furnace the whole process of fusion and fining of the glass goes on in this single chamber, and an endeavour is made to graduate the temperature of the furnace in a suitable manner from the hot end where the raw materials have to be melted down to the colder end where the glass must be sufficiently viscous to be gathered on the pipes. It is obvious that this control of the temperature cannot be so perfect in a furnace of the single chamber type as in one that is sub-divided. Such sub-divided furnaces are, as a matter of fact, much more frequent in sheet-glass practice; but this practice differs widely as to the manner and degree of the sub-division introduced. In the extreme form the glass practically passes through three independent furnaces merely connected with one another by suitable openings of relatively small area through which the glass flows from one to the other. If it were possible to build furnaces of materials that could resist the action of heat and of molten glass to an indefinite extent, it is probable that this extreme type would prove the best, since it gives the operator of the furnace the means of controlling the flow of glass in such a way that no unmelted material can leave the melting chamber and enter the fining chamber, and that no insufficiently fined glass can leave the fining chamber and find its way into the working chamber. But in practice the fact that this extreme sub-division introduces a great deal of extra furnace wall, exposed both to heat and to

contact with the glass, involves very serious compensating disadvantages—the cost of construction, maintenance and renewal of the furnace is greatly increased, while there is also an increased source of contamination of the glass from the erosion of the furnace walls. It is, therefore, in accordance with expectations to find that the most successful furnaces for the production of sheet-glass are intermediate in this respect between the simple open furnace and the completely sub-divided one. In some cases the working chamber is separated from the melting and fining chamber by a transverse wall above the level of the glass, while fire-clay blocks floating in the glass just below this cross wall serve to complete the separation and to retain any surface impurities that may float down the furnace.

As regards the depth of glass in the tank, practice also varies very much. The advantages claimed for a deep bath are that the fire-clay bottom of the furnace is thereby kept colder and is consequently less attacked, so that this portion of the furnace will last for many years. On the other hand the existence of a great mass of glass at a moderate heat may easily prove the source of contamination arising from crystallisation or "devitrification" occurring there and spreading into the hotter glass above. Also, if for any reason it should become necessary to remove part or all of the contents of the tank, the greater mass of glass in those with deep baths becomes a formidable obstacle. On the whole, however, modern practice appears to favour the use of deeper baths, depths of 2 ft. 6 in. or even 3 ft. being very usual, while depths up to 4 ft. have been used.

The question of the proper height of the "crown" or vault of the furnace is of considerable importance to the proper working of the tank. For the purpose of producing the most perfect combustion, it has been contended that a large free flame-space is required. The earlier glass-melting tanks, like the earlier steel furnaces, were built with very low crowns, forcing the flame into contact with the surface of the molten glass, the object being to

promote direct heating by immediate contact of flame and glass; for a time there was a strong tendency in the direction of higher crowns, leaving the heating of the glass to be accomplished by radiation rather than direct conduction of heat. There can be little doubt that up to a certain point the enlargement of the flame-space tends towards greater cleanliness of working, but if the height of a furnace crown be excessive there is a decided loss of economy. Flame-spaces as high as 6 ft. from the level of the glass to the highest part of the crown have been used, but the more usual heights range from 2 ft. to 4 ft.

The "ports" or apertures by which pre-heated gas and air enter the furnace chamber differ very widely in various furnaces. In some cases the gas and air are allowed to meet in a small combustion chamber just before entering the furnace itself, while in other cases the gas and air enter the furnace by entirely separate openings, only meeting in the furnace chamber. The latter arrangement tends to the formation of a highly reducing flame, which is advantageous for the reduction of salt-cake, but is by no means economical as regards fuel consumption. On the other hand, by producing a perfect mixing of the entering gas and air in suitable proportions, the other type of ports can be made to give almost any kind of flame desired, although their tendency is to form a more oxidising atmosphere within the furnace. The latter type of ports, although widely varied in detail, are now almost universally adopted in sheet tank furnaces.

All modern tank furnaces work on the principle of the recovery of heat from the heated products of combustion as they leave the furnace, and the return of this heat to the furnace by utilising it to pre-heat the incoming gas and air; but the means employed to effect the application of this "regenerative" principle differ considerably in various types of plant. Perhaps the most widely-used form of furnace is the direct descendant of the original Siemens regenerative furnace, in which four regenerator chambers are provided with means for reversing the flow of gas and air in such

a way that each pair of chambers serves alternately to absorb the heat of the outgoing gases and subsequently to return this heat to the incoming air that passes through one, and the incoming gas that passes through the other of these chambers. In these furnaces the regenerator chambers themselves are generally placed underneath the melting furnace, and they are built of fire-brick and filled with loosely-stacked fire-bricks, whose function it is to absorb or deliver the heat. In the most modern type of furnaces of this class the gas-regenerators are omitted entirely, the air only being pre-heated by means of regenerators, while the gas enters the furnace direct from the producer, thus carrying with it the heat generated in the producer during the gasification of the fuel. While this arrangement is undoubtedly economical, it has the serious disadvantage, especially in the manufacture of sheet-glass, that the gas, rushing direct from the producer into the furnace, carries with it a great deal of dust and ash, which it has no opportunity of depositing, as in the older types of furnace, in long flues.

The most serious disadvantages of the ordinary types of regenerative furnaces are due to the considerable dimensions of the regenerative apparatus, necessitating a costly form of construction and occupying a large space, while the necessity of periodically reversing the valves so as to secure the alternation in the flow of outgoing and incoming gases requires special attention on the part of the men engaged in operating the furnace, as well as the construction and maintenance of valves under conditions of heat and dirt that are not favourable to the life of mechanical appliances. It is claimed that all these disadvantages are overcome to a considerable extent in one or other of the various forms of furnace known as "recuperative." In these furnaces there is no alternation of flow, and the regenerator chambers are replaced by "recuperators." These consist of a large number of small flues or pipes passing through a built-up mass of fire-brick in two directions at right-angles to one another; through the pipes running in one direction the waste ases pass out to the chimney, while the incoming gas and air pass

through the other set of pipes. A transference of heat between the two currents of gas takes place by the conductivity of the fire-brick, and thus the outgoing gases are continuously cooled while the ingoing gases are heated—the transference of heat being somewhat similar to that which takes place in the surface condenser of a steam engine. Theoretically this is a much simpler arrangement than that of separate regenerator chambers, and to some extent it is found preferable in practice, but there are certain disadvantages associated with the system which arise principally from the peculiar nature of the material—fire-brick—of which the recuperators are generally constructed. In the first place, the heat-conductivity of fire-brick is not very high, so that, in order to secure efficiency, the recuperators must be large, and while the individual pipes must be of small diameter, their area as a whole must be large enough to allow the gases to pass through somewhat slowly. Next, owing to the tendency of fire-brick to warp, shrink and crack under the prolonged effects of high temperatures, it becomes difficult to prevent leakage of gases from one set of pipes into the other. If this occurs to a moderate extent its principal effect will be to allow some of the combustible gas to pass direct to the chimney, at the same time causing a dilution of the gases entering the furnace by an addition of products of combustion from the waste-gas flues. This, of course, tends to reduce the efficiency of the furnace and requires a higher fuel consumption if the temperature is to be maintained at its proper level. Ultimately the leakage reaches a point where re-construction of the furnace becomes necessary. It follows from these considerations that, although the recuperative furnace is somewhat simpler and cheaper to construct, it requires, if anything, more careful maintenance than the older forms of regenerative furnace.

Tank-furnaces for the production of sheet-glass in this country are generally worked from early on Monday morning until late on Saturday night, glass-blowing operations being suspended during Sunday, although the heat of the furnace must be maintained. On

the Continent, and especially in Belgium, the work in connection with these furnaces goes on without any intermission on Sunday—a difference which, however desirable the English practice may be, has the effect of handicapping the output of a British furnace of equal capacity by about 10 per cent. without materially lessening the working cost.

The ordinary process of blowing sheet-glass in an English glass-works is generally carried out by groups of three workmen, viz., a "pipe-warmer," a "gatherer," and a "blower," although the precise division of the work varies according to circumstances. The pipe-warmer's work consists in the first place in fetching the blowing-pipe from a small subsidiary furnace in which he has previously placed it for the purpose of warming up the thick "nose" end upon which the glass is subsequently gathered. The sheet-blower's pipe itself is an iron tube about 4 ft. 6 in. long, provided at the one end with a wooden sleeve or handle, and a mouthpiece, while the other end is thickened up into a substantial cone, having a round end. Before introducing the pipe into the opening of the tank-furnace, the pipe-warmer must see that the hot end of the pipe is free from scale or dirt and must test, by blowing through it, whether the pipe is free from internal obstructions. He then places the butt of the pipe in the opening of the furnace and allows it to acquire as nearly as possible the temperature of the molten glass. When this is the case the pipe is either handed on to the gatherer, or the pipe-warmer, who is usually only a youth, may take the process one step further before handing it on to the more highly skilled workman. This next step consists in taking up the first gathering of glass on the pipe. For this purpose the hot nose of the pipe is dipped into the molten glass, turned slowly round once or twice and then removed, the thread of viscous glass that comes up with the pipe being cut off against the fire-clay ring that floats in the glass in front of the working opening. A small quantity of glass is thus left adhering to the nose of the pipe, and this is now allowed to cool down until it is fairly stiff, the whole pipe being

meanwhile rotated so as to keep this first gathering nicely rounded, while a slight application of air-pressure, by blowing down the pipe, forms a very small hollow space in the mass of glass and secures the freedom of the opening of the pipe. When the glass forming the first gathering has cooled sufficiently, the gatherer proceeds to take up the second gathering upon it. The pipe is again introduced into the furnace and gradually dipped into the molten glass, but this must be done with great care so as to avoid the inclusion of air-bells between the glass already on the pipe and the new layer of hotter glass that is now taken up. This freedom from air-bells is secured by a skilful gatherer by a gradual rotation of the pipe as it is lowered into the glass, thus allowing the two layers of glass to come into contact with a sort of rolling motion that allows the air time to escape. When completely immersed, the pipe is rotated a few times and is then withdrawn and the "thread" again cut off. The mass of glass on the end of the pipe is now considerably larger than before and requires more careful manipulation to cause it to retain the proper, nearly spherical shape. During the cooling process which now follows the pipe is laid across an iron trough, kept brimful of water; this serves to cool the pipe itself, and also allows the pipe to be readily rotated backwards and forwards by rolling it a little way along the trough. When the whole mass of glass has again cooled sufficiently to be manipulated without risk of rapid deformation, a third gathering of glass is taken up, in precisely the same manner as that already described for the second gathering, and if the quantity of glass required is large, or the glass itself is so hot and fluid that only a comparatively small weight adheres at each time of gathering, the process may be repeated a fourth or even a fifth time, but as the weight of pipe and adhering glass increases with each gathering, each step becomes more laborious, while the hot glass, being now held on a much larger sphere, tends to flow off more readily, so that greater skill is required to avoid "losing" the gathering.

The care and skill with which these operations of gathering are

carried out determine, to a large extent, the quality of the resulting sheet of glass; any want of regularity in the shape of the gathering leads inevitably to variations of thickness in different parts of the sheet, while careless gathering will introduce bubbles or "blisters" and other markings. During the intermediate cooling stages the glass must be protected from dust and dirt of all kinds, since small specks falling upon the hot glass give rise to an evolution of minute gas bubbles which become painfully evident in the sorting room.

When the last gathering has been taken up and the mass cooled so far as to allow of its being carried about without fear of loss, the glass forms an approximately spherical mass, with the nose-end

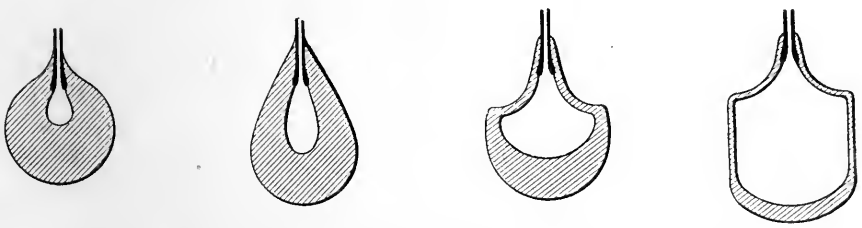

FIG. 14.—Early stages in the formation of cylinders for sheet-glass.

of the pipe at or near the centre of the sphere. The next stages of the process consist in the preliminary shaping of this mass in such a way as to bring the bulk of the glass beyond the end of the pipe, and then in forming just beyond the end of the pipe a widened shoulder of thinner and therefore colder glass, of the diameter required for the cylinder into which the glass is to be blown. This is done by bringing the glass into the successive shapes shown in Fig. 14, the forming of the glass being effected by the aid of specially shaped blocks and other shaping instruments in which the glass is turned and blown. The final shape attained at this stage is a squat cylinder containing the bulk of the glass at its lower end, and connected to the pipe by the thinner and colder neck and shoulder already mentioned.

At this point of the process the pipe with its adherent glass is

handed over to the blower proper. This operator works on a special stage erected in front of small furnaces, called "blowing holes," although in some works these are dispensed with, and the stages are erected in front of the melting furnace itself. The sheet-blower's stage is simply a platform placed over or at the side of a suitable excavation which gives the blower the necessary space to swing the pipe and cylinder freely at arm's length. The blowing process itself involves very little actual blowing, but depends rather upon

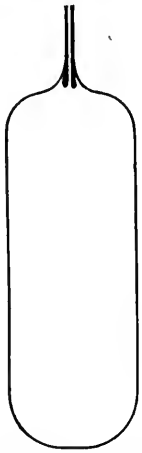

FIG. 15.—Later stage in sheet-glass blowing.

the action of gravitation and on centrifugal effects for the formation of the large, elongated cylinder from the squat cylinder with which the blower commences. The process consists in holding the thick, lower end of the cylinder in the heating-furnace, and when sufficiently hot, withdrawing it and swinging the pipe with a pendulum movement in the blower's pit. The cylinder thus elongates itself under its own weight, and any tendency to collapse is counteracted by the application of air-pressure by the mouth, the pipe being also, at times, rotated rapidly about its own axis. The re-heating of the lower end of the cylinder is repeated several times, until finally the glass has assumed the form of a cylinder of equal thickness all

over, but closed with a rounded dome at the lower end (Fig. 15). This rounded end is now opened. In the case of fairly thin and light cylinders this is done by holding the thumb over the mouthpiece of the pipe in such a way as to make an air-tight seal, and then heating the end of the cylinder in the blowing-hole. The heat both softens the glass at the end and at the same time causes considerable expansion of the air enclosed in the cylinder, with the result that the end of the cylinder is burst open. After a little further heating, during which the glass at the end of the cylinder becomes very soft, and takes a wavy, curly shape, the blower withdraws the cylinder from the furnace, and holding it vertically downwards in his pit, spins it rapidly about its longitudinal axis. The soft glass at the lower end immediately opens out under the centrifugal action, and the blower increases the speed of rotation until the soft glass has opened out far enough to form a true continuation of the rest of the cylinder, and in this position it is allowed to solidify. With thick, heavy cylinders the first opening of the end is done in a different way. A small quantity of hot glass is taken up by an assistant on an iron rod, and is laid upon the centre of the closed end of the cylinder. The heat of this mass of hot glass softens the glass of the cylinder, and the operator, with the aid of a special pair of shears, cuts out a small circle of this softened glass, thus opening the end. The final operation of straightening out the opened end is carried out in the same way as described above for lighter cylinders.

The completed cylinder, still attached to the pipe, is now carried away from the blowing-stage and laid upon a wooden rack; then the blower takes up a piece of cold iron, and placing it against the neck of glass attaching the cylinder to the pipe, produces a crack; a short jerk then serves completely to sever the pipe from the cylinder. A boy now takes the pipe to a stand where it is allowed to cool and where the adhering glass cracks off from it prior to passing it back to the pipe-warmer for fresh use.

On the wooden rack the cylinder of glass is allowed to cool to

a certain extent, and then the remaining portion of the neck and shoulder (see Fig. 15) are removed. This is done by a boy who passes a thread of soft, hot glass around the cylinder at the point where it is to be cut off; the thread of hot glass merely serves to produce intense local heating, for as soon as it has become stiff the thread of glass is pushed off and a cold or moist iron is applied to the cylinder at the point where it had been heated by the thread. As a rule a crack immediately runs completely round the cylinder along the line of the thread, and the "cap" is thus removed. The glass is now in the form of a uniform cylinder open at both ends, but it must be opened out into a flat sheet before it can assume the familiar form of sheet-glass.

The first stage in the opening-out process is that of splitting. For this purpose the cylinders are carried to a special stand, upon which they are laid in a horizontal position, and here a crack or cut is made along one of the generating lines of the cylinder. This may be done either by the application of a hot iron, followed, if necessary, by slight moistening, or by the aid of a cut from a heavy diamond drawn skilfully down the inside of the cylinder. It will be seen from the account of the process so far given that the glass has as yet undergone no real annealing, although the blower is expected to "anneal" his cylinder during the blowing process, as far as possible, by never allowing it to cool too suddenly, and this degree of annealing is usually sufficient to save the cylinder from breaking under its internal stresses when left to cool on the racks. The surface of the glass, however, is left in a decidedly hardened condition, especially on the outside, which has necessarily been most rapidly cooled. For this reason—among others—the splitting cut is always made on the inside of the cylinder. The difference between the rates of cooling of the outside and inside of the cylinder has a further effect, which becomes evident as soon as the cylinder is split. The outside having become hard while the inside was still relatively soft, the outer layers of glass are in a state of compression and the inner layers in a state of tension in the cold

cylinder. As soon as the cylinder is split, however, these stresses are to some extent relieved, the inner layers being then free to contract and the outer layers to expand; the result is an increase in the curvature of the cylinder, which slightly decreases in diameter, the cut edges overlapping. If the cylinder has been cooled rather too quickly, or if the glass itself has a high co-efficient of expansion, this release of internal stresses at the moment of splitting becomes very marked, and each cylinder splits with the sound of a small explosion, while if the internal stresses are still more severe, the cylinders may even fly to pieces as soon as they are cut.

The next stage in the manufacture of a sheet of glass is the flattening and annealing process. For this purpose the split cylinders are taken to a special kiln, generally known as a "lear," or "lehr," where they are first of all raised to a dull red-heat; they are then lifted, one at a time, on to a smooth stone or slab placed in a chamber of the kiln where the heat is great enough to soften the glass. Here the cylinder is laid down with the split edges upwards, and by means of a wooden tool the glass is slowly spread out, being finally rubbed down into perfect contact with the slab or "lagre." From the flattening slab the sheet as it now is passes into the annealing kiln, which communicates with the flattening chamber. This consists, similarly to other continuous annealing kilns already described in connection with other varieties of glass, of a long tunnel, heated to the temperature of the flattening kiln at one end and nearly cold at the other. The sheets are moved down this tunnel at a uniform slow rate by the action of a system of grids which, at intervals, lift the sheets from the bottom of the kiln, move them forward by a short distance, and again deposit them on the bottom, the grids themselves returning to their former position by a retrograde movement made below the level of the kiln-bottom, and therefore not affecting the glass.

On leaving the annealing kiln the sheets of glass are sometimes covered with a white deposit arising from the products of combustion in the kiln and their interaction with the glass itself. This

deposit can be removed by simple mechanical rubbing, but it is usual to dip the glass into a weak acid bath, which dissolves the white film and leaves the glass clear and bright, ready for use.

From the annealing kiln the finished sheets of glass are taken to the sorting-room, where they are examined in a good light against a black background, and are sorted according to their quality for different purposes.

The defects which are found in sheet-glass are of a very varied nature, as would be anticipated from the long and complicated process of manufacture which the material undergoes in the course of its transformation from the raw material into the finished sheet of glass. A full enumeration of all possible defects, with their technical names, need not be given here, but a description of the more important and frequent ones will be useful. The defects may be conveniently grouped according to the stage of the process from which they originate.

The first class of defects accordingly embraces those that arise from the condition of the glass as it exists in the working-end of the furnace. Chief of these are white opaque enclosures, known as "stones." These may arise from a variety of causes within the furnace, such as an admixture of infusible impurities with the raw materials, insufficient heat or duration of melting, leading to a residue of unmelted raw material in the finished glass, or from defective condition of the interior of the furnace, leading to contamination of the glass with small particles of fire-brick. Further, if any part of the furnace has been allowed to remain at too low a temperature, or if the composition of the glass is unsuitable, crystallisation may occur, and white patches of crystalline material may find their way into the finished sheets. Another defect that may arise from the condition of the glass in the furnace is the presence of numerous small bubbles, known as "seed." By the blowing process these are drawn out into pointed ovals, and they are rarely quite absent from sheet-glass. They arise from either incomplete fining of the glass in the furnace or from allowing the glass to come

into contact with minute particles of dust during the gathering process. Another possible defect to the glass itself may be found at times in too deep a colour. This is only seen readily when a sheet of some size is examined edgewise, as most varieties of ordinary sheet-glass are too free from colour to allow this to be judged by looking through the sheet in the ordinary way. It follows from this fact that for practical purposes, where the light always traverses one thickness of the glass only, a slight difference of colour should be regarded as a very minor consideration, at all events as compared with freedom from other defects.

The gathering process in its turn is responsible for further defects of sheet-glass. Some of these, such as defects arising from the use of a dirty pipe, are never allowed to pass beyond the sorting-room, and are therefore of no interest to the user of glass. Of those whose traces are seen in the glass that passes into use, "blisters" and "string" are the most important. "Blisters" are somewhat larger, flat air-bells, arising from the inclusion of air between successive layers of the gathering. "String" is a very common defect in all sheet-glass. To some extent it may arise from want of homogeneity in the glass itself. If this consists of layers of different densities and viscosities, the gatherer will take these up on his gathering, and ultimately they will form thickened ridges of glass running around the cylinders and across the sheets. Such striæ, due to want of homogeneity in the glass, are much more common in flint glass than in the soda-lime glasses used for sheet manufacture, but are not unknown in the latter. On the other hand, even if the glass be as homogeneous as possible, the gatherer can produce these striæ if he takes up his glass from a place close to the side of the fire-clay ring that floats in the furnace in front of his working opening. Glass always acts chemically upon fire-clay, gradually forming a layer of glass next to the fire-clay that contains much more alumina than the rest of the contents of the furnace. Such a layer is formed on the surface of each ring in a sheet tank, but if the gathering is taken from the centre of the ring, this

layer of aluminiferous glass remains undisturbed. If, however the gatherer brings his pipe too near the side of the ring, the glass will draw some of this different layer on to the gathering, and this glass will form thick ridges and striæ running across the sheet in all directions. Another defect for which the gatherer is generally responsible is that of variation of thickness within the same sheet. The blower, however, can also produce this defect.

During the blowing proper a further series of defects may be introduced, principally by allowing particles of glass derived from certain stages of the process to fall upon the hot glass of the cylinder and there become attached permanently. More serious, and also more frequent, is the greater or less malformation of the cylinder. If the glass as it leaves the blower is of any shape other than that of a true cylinder, it becomes impossible to spread it into a truly flat sheet in the flattening kiln. Sometimes, in practice, the "cylinder" is wider at one end than at the other, or, worse still, it is of uneven diameter, showing expanded and contracted areas alternately. When such a cylinder comes to be spread out on the slab it cannot be flattened completely, and various hollows and hillocks are left, which mar the flatness of the sheet and interfere with the regular passage of light through it when in use.

Finally, the process of flattening is apt to introduce defects of its own. The most common of these are scratches arising from marks left by the flattening tool; indeed, in all sheet-glass it is quite possible to see, by careful examination of the surfaces, upon which side the flattening tool was used. Sheet-glass thus has one side decidedly brighter and better in surface than the other, the better side being that which rested upon the "lagre" during the flattening process. On the other hand, if the slab itself be not quite perfect, or if any foreign body be allowed to rest upon it, that side of the glass will be marked in a corresponding manner.

In the account of the manufacture of sheet-glass given above, we have outlined one typical form of the process, but nearly every stage is subject to modifications according to the practice and

particular circumstances of each works. We will now describe one or two special modifications that are of more general importance.

First, as regards the melting process, although the tank-furnace has almost entirely superseded the pot-furnace for the production of ordinary sheet-glass, there are still some special circumstances under which the pot-furnace is capable of holding its own. Thus, where for special purposes it is desired to produce a variety of sheet-glass which, as regards all defects arising out of the glass itself, and especially as regards colour, is required to be as perfect as possible, melting in pots is found advantageous, and for some very special purposes even covered (hooded) pots are used. For such special purposes, too, sulphate of soda is eliminated from the raw materials and carbonate of soda (soda ash) substituted. For the production of tinted glasses also, whether they are tinted throughout their mass, or merely covered with a thin layer of tinted glass ("flashed"), manufacture in pot- rather than tank-furnaces is generally adopted, the exact nature and composition of the glass being far better under control in the case of pots.

The blowing process is also subject to wide variations of practice. The most important of these variations concerns the shape and dimensions of the cylinders. In English and Belgian works the dimensions of the cylinders are so chosen that the length of the cylinder constitutes the longest dimension of the finished sheet, the diameter of the cylinder forming the shorter dimension. In some parts of Germany, however, the practice is the reverse of this, the cylinders being blown shorter and much wider, so that the circumference of the cylinder constitutes the longest dimension of the finished sheet. It is, however, pretty generally recognised that the latter method has very serious disadvantages, although it is claimed that somewhat more perfect glass can be obtained by its means. For the production of a special variety of glass, known as "blown plate-glass," this method of blowing short wide cylinders is still adhered to. This is a very pure form of sheet-glass, blown into thick, small sheets which are subsequently ground and polished in

the same manner as plate-glass. Here the great thickness of glass required seems to render the blowing of long cylinders very difficult, and the other form is therefore adopted. On the other hand, English patent plate-glass, which is made by grinding and polishing the best quality of ordinary sheet-glass, is made from glass blown into long narrow cylinders in the manner described in detail above.

The process of blowing described above is capable, with slight modifications, of yielding glass with surfaces other than the plain smooth face of ordinary sheet-glass. Thus fluted and "muffled" glass are produced in a very similar manner to that described above for ordinary sheet, except that the fluting or the irregular surface markings which constitute the peculiarities of these two varieties of glass, are impressed upon the surface of the cylinder at an early stage in the process.

From the outline description given above of the usual method of manufacture of sheet-glass, it will readily be seen that this is a long, complicated, and laborious process, requiring the employment of much skilled labour, and involving the production of a relatively complicated form, viz., the closed cylinder, as a preliminary to the production of a very simple form, viz., the flat sheet. It is therefore by no means surprising to find that a great many inventors have worked and are still working at the problem of a direct mechanical method of producing flat glass possessing a natural "fire polish" at least equal to that of ordinary sheet-glass. The earlier inventors have almost uniformly endeavoured to attain this object by attempting to improve the process of rolling glass, with a view to obtaining rolled sheets having a satisfactory surface. We have already indicated why these efforts have never met with success and what reasons there are for believing that they are never likely to attain their object. A totally different line is that taken by Sievert, to whose inventions we have already referred in connection with the mechanical production of blown articles. This inventor has endeavoured to utilise his process for blowing large articles of glass for the direct production of sheets

of flat glass. His method is to blow, by the steam process described in another chapter, a large cubical vessel, having flat sides, the flatness of these sides being ensured by blowing the vessel into or against a mould having flat sides. This flat-sided vessel is ultimately to be cut up into five large sheets. This process also appears to involve some of the main difficulties of rolling as regards the means of transferring the glass from the furnace to the plate of the blowing machine, and in practice the inventor has not yet succeeded in producing glass of sufficiently good surface for the purposes of sheet-glass.

Another class of processes entirely avoid all means of transferring molten glass from the furnace to any machine by working on glass direct from the molten bath itself. Some of these processes are in actual use in America, and others are being tried in Europe; there can, however, be little doubt that they have overcome the greatest of the many difficulties that stood in the way of the mechanical production of sheet-glass, and that they are therefore destined very shortly to supersede the hand process.

One of the earliest of these direct processes proposed to allow the molten glass to flow out from the furnace, downward, through a narrow slit formed in the side or bottom of the tank. The impossibility of keeping such a narrow orifice open and at the same time regulating the flow of glass made this proposal impracticable, although the use of drawing orifices has been revived in one of the latest processes.

The American process, which has now been at work under commercial conditions for a number of years, is not entirely satisfactory in this respect—that it is a mechanical process for the production of cylinders and not of flat sheets, so that the subsidiary processes of splitting and flattening still remain to be carried out as before.

In one form of this process, which is known as the Frinck system, the glass is first transferred from the melting tank into a special furnace or basin in which a vertical fire-clay tube passes through the bath of molten glass from below upwards. The glass is allowed

to fine or "settle" after ladling into this basin, and then the drawing operation is carried out. For this purpose an iron "bait" or cover, which has previously been electrically heated to the right temperature, is lowered into the molten glass, and is then steadily raised. The glass adheres to the "bait" and is drawn up with it. But if the cylinder thus formed were left unsupported, it would tend to contract and would soon be "drawn off" to a point. This tendency is avoided by blowing compressed air into the rising cylinder as it is formed, through the fire-clay tube already mentioned. This use of internal pressure is found to be superior to the earlier device of chilling the cylinder as it emerged from the surface of the molten glass by means of jets of cold air. When the cylinder has been drawn to the desired length, the rate of raising is increased and the air-pressure adjusted in such a way that the cylinder "draws off." The whole long cylinder is then placed in a horizontal position, is detached from the "bait," and is then cut up into lengths before being split and flattened in the ordinary way.

The inventions of Fourcault aim at a much more direct process. Here also the glass is drawn direct from the molten bath by the aid of a drawing-iron that is immersed in the glass and then slowly raised, but in this case the piece immersed is simply a straight bar, and the aim is to draw out a flat sheet. In this case the tendency, under surface tension, is to contract the sheet into a thread, and apparently the simple device of chilling the emerging glass is not adequate to prevent this in a satisfactory manner, and subsidiary devices have been added. Those that have been patented include a mechanism of linked metal rods so arranged as to be immersed and drawn out of the glass continuously with the emerging sheet, in such a manner as to support the vertical edges of the glass and so aid in resisting the tendency of the glass to contract laterally. Another device consists in the use of a slit or orifice formed in a large fire-brick that floats on the surface of the glass. Through this orifice the glass is drawn, of the desired thickness and width. The

use of this orifice, however, interferes markedly with the perfection of the product, and in fact all the glass produced in this way shows quite plainly a set of longitudinal striations due to the inevitable irregularities in the lips of the drawing slot. Further, it appears to be impracticable to draw *thin* glass in this way, a thickness of from $2\frac{1}{2}$ to 3 millimetres (about $\frac{1}{8}$ inch) being the least that is practicable, on account of the large amount of breakage that occurs with weaker sheets. This process, in its present stage of development, however promising, does not appear to have solved the problem of mechanical manufacture of sheet-glass, since it is just in the thinner, lighter kinds of glass that the advantages of sheet are most pronounced. On the other hand, it is quite possible that this drawing process, or some development arising from it, may shortly supplant the casting process in the production of polished plate-glass, although for the largest sizes of this product also, the difficulty and danger of handling the weights involved may prove a serious obstacle. More recently, both these direct drawing devices and the closely allied "flow" devices in which the glass is allowed to flow in a thin stream or sheet over a suitably prepared ledge or "weir" have been much developed in America, notably by Owens and his collaborators, whose successful bottle-blowing machines have already been referred to. In Colburn's patented method, which is being developed by Owens, the glass is drawn direct from the furnace in a continuous sheet through the lear, the resulting sheets reaching a length up to 200 feet. Whether the product of this operation is of a quality capable of fulfilling the requirements of good sheet-glass is not yet certain.

Crown Glass.—Although this is a branch of manufacture that is nearly obsolete it deserves brief notice here, partly because it is still used for the production of special articles, and also because it illustrates some interesting possibilities in the use and manipulation of glass.

The process of blowing crown glass may be briefly described as that of first blowing an approximately spherical hollow ball, then

opening this at one side and expanding the glas into a flat disc by the action of centrifugal forces produced by a rapid rotation of the glass in front of a large opening in a special heating furnace. The actual process involves, of course, the preliminary of gathering the proper quantity of glass, much in the manner already described in connection with sheet-glass manufacture. This gathering is then blown out into a hollow spherical vessel. This vessel is now attached to a subsidiary iron rod by means of a small gathering of hot glass, applied at the point opposite the pipe itself, the glass being thus, for a moment, attached to both the pipe and the "pontil" or "punty" (as the rod is called). The pipe is, however, detached by cracking off the neck of the original glass, which now remains attached to the pontil in the shape of an open bowl. This bowl is now re-heated very strongly in front of a special furnace, the open side of the bowl being presented to the fire. The pontil is meanwhile held in a horizontal position and rotated. As the glass softens the rotation spreads it out, until finally the entire mass of glass is formed into a simple flat disc spinning rapidly before the mouth of the furnace. This flat disc or "table" of crown glass is allowed to cool somewhat, is detached from the pontil by a sharp jerk, and is then annealed in a simple kiln in which the glass is stacked, sealed up, and allowed to cool naturally.

It is obvious that by this process no very large sheets of glass can be produced; tables 4 ft. in diameter are already on the large side, and these can only be cut up into much smaller sheets on account of the lump of glass by which the table was originally attached to the pontil, and which remains fixed in the centre of the finished disc. For certain ornamental purposes, where an "antique" appearance is desired, these bullions are valued, but for practical purposes they interfere very seriously with the use of the glass. As a matter of fact, even several inches away from the central bullion itself, crown glass is generally marked with circular wavings, which render it readily recognisable in the windows of older buildings, but which decidedly detract from the perfection of the glass.

On the other hand, crown glass is still valued for certain purposes, such as microscope slides and cover glasses, where entire freedom from surface markings, such as those found in sheet-glass as a result of the flattening operations, is desirable. While, therefore, the process has merely an historical interest so far as ordinary sheet-glass purposes are concerned, it is still used in special cases.

CHAPTER XII

COLOURED GLASSES

In various chapters throughout the foregoing portions of this book we have had occasion to refer to the colour of glass and the causes affecting it, but these references have chiefly been made from the point of view of the production of glasses as nearly colourless as possible under the circumstances. While it is obvious that for the great majority of the purposes for which it is used the absence of all visible coloration is desirable or even essential in the glass employed, there are numerous other uses where a definite coloration is required. Thus we have, as industrial and technical uses of coloured glass, the employment of ruby, green and purple glasses for signalling purposes, as in the signal lamps of our railways, the red tail-lights of motor-cars, or even the red or green sectors of certain harbour lights and lighthouses; again, coloured glasses, ruby, green, and yellow, are extensively employed in connection with photography. Rather less exacting in their demands upon the correctness of the colour employed are the architectural and ornamental uses to which coloured glass is so extensively put in both public and domestic buildings, while, finally, coloured glass is largely the foundation upon which the stained-glass worker builds up his artistic achievements; in another direction, coloured glass is also utilised in the production of ornamental articles and of some table-ware. While it must be admitted that in a great many cases the colour-resources of the glass-maker are hopelessly misapplied, yet in really artistic hands few other materials are capable of yielding results of equal beauty.

By the "colour" of a glass is generally understood the tint or

colour which is observed when it is viewed, in comparatively thin slices, by transmitted light; the actual colour is thus a property, not so much of the kind or variety of glass as of each individual piece, since thick pieces out of the same melting will show a different tint from that seen in thinner pieces. As we have already pointed out, such glasses as sheet or plate, which appear practically colourless when viewed in the ordinary way, show a very decided green colour when viewed through a considerable thickness. In the same way a very thin layer of the glass known as "flashing ruby" shows a brilliant red tint, but a thickness of one-sixteenth of an inch is sufficient to render the glass practically opaque, giving it a black appearance by both transmitted and reflected light. Again, cobalt blue glass, when examined with a spectroscope in thin layers, is found to transmit a notable proportion of red rays, but thicker pieces entirely suppress these rays. These phenomena will be readily understood when we recollect that colour in a transparent medium arises from the fact that the medium has different absorbing powers for light of different colours. All transparent substances, and certainly glass, are only *partially* transparent: all light waves passing through such a substance are gradually absorbed, and the extent to which they are absorbed differs according to the length of these waves. It always happens that for some special wave-lengths the substance has the power of absorbing the energy of the entering waves and converting it into heat-vibrations of its own molecules or atoms. In the most transparent and colourless glasses this process, so far as the waves of ordinary light are concerned, only goes on to a negligibly slight extent; if, however, we extend our view beyond the range of ordinary visible light, and consider the region of shorter waves that lies in the spectrum beyond the violet, we find that ordinary colourless glass becomes strongly absorbent; thus to waves of about half the length of those which produce upon our eyes the impression of yellow light, ordinary glass is as opaque as is a piece of metal to white light. In this wider sense, then, we may fairly say that all glasses are coloured—

i.e., all have a power of selective absorption; but in the case of those which are nearly colourless in the ordinary sense, this absorption takes place only for waves which are either decidedly shorter or decidedly longer than those to which our eyes are sensitive. Those glasses which appear coloured in the ordinary sense, on the other hand, owe this property to the fact that the power of absorption for light-waves extends into the region of the visible spectrum; thus a blue or violet glass is practically opaque to red rays, while a red glass is opaque to blue, green or violet rays. This statement may be verified in a striking manner by holding over one another a piece of deep blue or green glass and a piece of deep ruby glass—the combination will be found to be very nearly opaque even when each glass by itself is practically transparent.

The question which now naturally presents itself to us is, what is the essential difference between, for instance, a piece of red glass and a piece of "white" glass that confers upon the former the power of absorbing blue light? A perfectly complete and satisfactory answer to this question is not, in the writer's opinion, available in the present state of our knowledge, but to a certain extent the difference between the two kinds of glass can be explained. The difference is *produced*, in the first instance, by introducing into the colourless glass some additional chemical element or elements, the substances in question being generally known as "colouring oxides," although they are by no means always introduced in the form of oxides, and are frequently present in the glass in entirely different forms. To a certain extent the colour of the glass may be ascribed to a definite "colouring" property of the chemical elements concerned; thus most of the chemical compounds of such elements as nickel, cobalt, iron, manganese and copper are more or less deeply coloured substances, and it would seem as if the atoms or "ions" of these elements had the specific power of absorbing certain varieties of light-waves while not materially affecting others. But this specific "colouring" property is not so easily explained when we recollect that the colours of iron compounds,

for example, may be green or red according to the state of combination in which that element is present, and that iron has also the power of imparting either a green or a yellow colour to glass according to circumstances. The detailed discussion of these questions, however, lies outside our present scope, and we must confine ourselves to the broad statement that colouring substance in glass may be roughly divided into two kinds or groups; the first and probably the largest group are those bodies which occur in glass in true solution, the element itself being present in the combined state as a silicate or other such compound (borate, phosphate, etc.) which is soluble in the glass. In this class the colouring effect upon the glass is specifically that of the element introduced, and is brought about in the same way as the colouring of water when a coloured salt—such as copper sulphate—is dissolved in it. The second class of colouring substances, however, behave in a different manner; they are probably present in the glass in a state of extremely fine division, and held not in true solution, but really in a sort of mechanical suspension that approximates to the condition of what is known as a "colloidal solution." The point which is known beyond doubt, thanks to the researches of Siedentopf and Szigmondi on ultra-microscopical particles, is that in certain coloured glasses, of which ruby glass is the best example, the colouring substance, be it gold or cuprous oxide, is present in the form of minute but by no means atomic or molecular particles suspended in the glass. The presence of these particles has been made optically evident, although it can hardly be said that they have been rendered visible, and it is at all events probable that these suspended particles act each as a whole in absorbing the light-waves characteristic of the colour which they produce in glass. This being the case, it is easy to understand how readily the colour of such glasses is altered or spoilt by manipulations which involve heating and cooling at different rates—too rapid a rate of cooling producing a different grouping of the minute particles, altering their size or shape, or even obliterating them entirely by allowing

the element in question to go into or to remain in solution in the glass.

While it would be entirely foreign to the purpose of this volume to give in this place a series of recipes for the production of various kinds of coloured glass, it will be desirable to state in general terms the colours or range of colours which can be produced in various kinds of glass by the introduction of those chemical elements which are ordinarily used in this way. In general terms it may be said that the lighter elements do not as a rule tend to the production of coloured glasses, while the heavier elements, so far as they can be retained in the glass in either solution or suspension, tend to produce an intense colouring effect. The element lead appears to form a striking exception to this rule, but this is due to the fact that while the silicates of most of the other heavy elements are more or less unstable, the silicate of lead is very stable, and can only be decomposed by the action of reducing agents. When lead silicates are decomposed in this way, however, the resulting glass immediately receives an exceedingly deep colour, being turned a deep opaque black, although in very thin layers the colour is decidedly brown. On the other hand, glasses very rich in lead are always decidedly yellow in colour, and it has been shown that this coloration is due to the natural colour of lead silicates and not to the presence of impurities. What has just been said of lead applies, with only very slight modification, also to the rare metal thallium and its compounds, which have been introduced into glass for special purposes. Leaving these two exceptional bodies on one side, we now pass to a consideration of the elements in the order of their chemical grouping. The rare elements will not be considered except in certain cases where their presence in traces is liable to affect results attained in practice.

The *Alkali Metals*, sodium, potassium, lithium, etc., and their compounds, have no specific colouring effect, although the presence of soda or of potash in a glass affects the colours produced by such substances as manganese, nickel, selenium, etc.

Copper, as would be anticipated from the deep colour of most of its compounds, produces powerful colouring effects on glass. Cupric silicates produce intense green, to greenish-blue tints. Copper, either as metal or oxide, added to glass in the ordinary way, always produces the green colour; but when the full oxidation of the copper is prevented by the presence of a reducing body, and the glass is cooled slowly, or is exposed to repeated heating followed by slow cooling, an intense ruby coloration is produced. In practice this colour is produced by introducing tin as well as copper into the mixture, and so regulating the conditions of melting as to favour reduction rather than oxidation of the copper. Under these circumstances the copper is left in the glass in a finely divided and evenly suspended state; if exactly the right state of division and suspension is arrived at, a beautiful red tint is the result, although the coloration of the glass is so intense that it can only be employed in very thin sheets, being "flashed" upon the surface of colourless glass to give it the necessary strength and thickness for practical use. It is further very easy slightly to alter the arrangement of the copper in the glass, with the result of producing an opaque, streaky substance resembling sealing-wax in colour and appearance, this product being, of course, useless from the glass-maker's point of view. Finally, by exceedingly slow cooling, and under other favouring conditions which are not really understood, the particles of suspended colouring-material—be it metallic copper or cuprous oxide—grow in size and attain visible dimensions, appearing as minute shimmering flakes, thus producing the beautiful substance known as "aventurine."

Silver is rarely introduced into glass mixtures, the reason being that it is so readily reduced to the metallic state from all its compounds that it cannot easily be retained in the glass except in a finely-divided form, causing the glass to assume a black, metallic appearance resembling the stains produced by the reduction of lead in flint glasses. On the other hand, silver yields a beautiful yellow colour when

applied to glass as a surface stain, and it is widely used for that purpose.

Gold is introduced into glass for the production of brilliant ruby tints; its behaviour is very similar to that of copper, except that the noble metal has a great tendency to return to the metallic state without the aid of reducing agents. No addition of tin is therefore required, but the rate of cooling, etc., must be properly regulated, since rapidly cooled glass containing gold shows no special colour, the rich ruby tint being only developed when the glass is re-heated and cooled slowly. The colouring effect of gold is undoubtedly more regular and uniform than that of copper, and it is accordingly possible to obtain much lighter shades of red with the aid of the noble metal. "Gold ruby" can therefore be obtained of a tint light enough to be used in sheets of ordinary thickness, and the process of "flashing" is not essential.

The elements of the second group, such as magnesium, calcium, strontium, barium, zinc and cadmium, exert no strong specific colouring action on glass, with perhaps the exception of cadmium, and that element only does so to any considerable extent in combination with sulphur, sulphide of cadmium having the power of producing rich yellow colours in glass. The sulphur compounds of barium also readily produce deep green and yellow colours, and the formation of these tints is, indeed, very difficult to avoid in the case of glasses containing much barium. A colouring effect has sometimes been ascribed to zinc, but this is not in accordance with facts.

Of the elements of the third group, only boron and aluminium are ever found in glass in any notable quantity. Boron is present in the form of boric acid or borates, and as such produces no colouring effect, nor does there seem to be any tendency for the separation of free boron. The compounds of aluminium also possess no colouring effect, although some compounds of this element are utilised for imparting a white opacity to glass for certain purposes—such glass being known as "opal."

The elements of the fourth group are of greater importance in connection with glass. Carbon is capable of exerting powerful colouring effects when introduced into glass. These effects are of two kinds, viz., indirect in consequence of the reducing action of carbon on other substances present, and direct from the presence of finely-divided carbon or carbides in the glass. The latter are similar in kind to those produced by the presence of other finely-divided elementary bodies (copper, gold, lead, etc.), except that the lightness of the carbon particles tends to the production of yellow and brown colours rather than of red and black, while the chemical nature of carbon renders the glass in which it is suspended indifferent to rapid cooling, so far as the carbon tint is concerned. The indirect effects of carbon, in reducing other substances that may be present in the glass, become evident with much smaller proportions of carbon than are required to produce visible direct effects. As we have seen above, carbon, in the form of coke, charcoal or anthracite coal, is regularly introduced, as a reducing medium, into glass mixtures containing sulphate of soda. If even a slight excess of carbon be used for this purpose, the formation of sulphides and poly-sulphides of sodium and of calcium results, and these bodies, like all sulphides, impart a greenish-yellow tint to the glass, at the same time bringing other undesirable results in their train.

Silicon, in the form of silicic acid and its compounds, is a fundamental constituent of all varieties of glass, and in this form is in no sense a colouring substance; on the other hand, there is no doubt that under some conditions silicon may be reduced to the metallic state at temperatures which normally occur in glass-furnaces, and it is practically certain, that if present in glass in this condition, silicon would colour the glass. It is just possible that some of the colouring effects produced in ordinary glass by powerful reducing agents, such as carbon, either in the solid form or as a constituent of furnace gases, may be due to the reduction of silicon in the glass.

Tin by itself does not appear to have any colouring effect upon

glass, except that its oxide, in a finely suspended state, produces opalescence and, in large quantities, white opacity. Tin, however, is used in conjunction with copper in the production of copper-ruby, to which reference has already been made.

Lead and Thallium have already been dealt with, and it only remains to add that their presence in the glass, although not in itself producing any intense colouring action, increases the colouring effects of other substances. This is probably merely a particular case of the fact that dense glasses, of high refractive index, are more sensitive to colouring agencies than the lighter glasses of low refractive index; this applies to barium as well as to lead and thallium glasses.

Phosphorus occurs in some few glasses in the form of phosphoric acid, and this substance, as such, has no colouring effect. Calcium phosphate, however, is sometimes added to glasses for the purpose of producing opalescence. Its action in this respect is probably similar to that of tin oxide and aluminium fluoride, these substances all remaining undissolved in the glass in the form of minute particles in a finely divided and suspended state.

Arsenic does not exert a colouring effect on glass, and owing to its volatile nature it can only be retained in glass in small quantities and under special conditions. A "decolourising" action is sometimes ascribed to arsenic, but if this action really exists it can only be ascribed to the fact that arsenic compounds are capable of acting as carriers of oxygen, and their presence thus tends to facilitate the oxidation of impurities contained in the glass. A further reference to this subject will be found below in reference to the compounds of manganese.

Antimony, although frequently added to special glass mixtures, does not appear to produce any very powerful effects, except possibly in the direction of producing white opacity if present in large proportions. The sulphide of antimony, however, exerts a colouring influence, although its volatile and unstable character renders the effects uncertain.

Vanadium, owing to its rarity, is probably never added to glass mixtures for colouring purposes, although it is capable of producing vivid yellow and greenish tints when present even in minute proportions. On the other hand, vanadium occurs in small proportions in a number of fire-clays, including some of those of the Stourbridge district, and glass melted in pots containing this element is liable to have its colour spoilt by taking up the vanadium from the clay.

Sulphur is an element whose presence in various forms is liable to affect the colour of glass in a variety of ways. The colouring effects of sodium-, calcium-, cadmium-, and antimony-sulphides have already been referred to. Sulphur probably never exists in glass in the uncombined state at all, but sulphur and its oxides, which are often contained in furnace gases, sometimes exert a very marked action upon hot glass. The presence of sulphur gases in the atmospheres of blowing-holes and annealing kilns is liable to produce in the glass a peculiar yellowish milkiness which penetrates for a considerable depth into the mass of the glass and cannot be removed by subsequent treatment. Glass vessels, particularly if made of glass produced from raw materials among which salt-cake has figured, are also affected by contact with fused sulphur or its vapour, the effect being a gradual disintegration of the glass. The precise mechanism of these actions is not known at present, but they probably consist in the formation of sulphur compounds within the glass, possibly giving rise to an evolution of minute bubbles of gas.

Selenium, which is chemically so closely related to sulphur, is a relatively rare element, which is, however, finding some use in glass-manufacture as a colouring and a decolouring agent. The introduction of selenium or of its compounds under suitable conditions into a glass mixture produces or tends to produce a peculiar yellowish-pink coloration, the intensity of the colour produced being dependent upon the chemical nature of the glass as a whole and, of course, upon the amount of selenium left in the glass at the end of the melting process, this latter in turn depending upon the

duration and temperature of the process in question. The pink colour of selenium glass is best developed in those containing barium as a base, but it is also developed in lead glasses, while soda-lime glasses do not show the colour so well. As a "decolouriser" the action of selenium is entirely that of producing a complementary colour which is intended to "cover" the green or blue tint of the glass; where the depth of the tint to be "covered" is small, selenium can be used very successfully in this way, although it is a relatively costly substance for such a purpose. No oxidising or "cleansing" action can be ascribed to selenium or its compounds.

Chromium is one of the most intensely active colouring substances that are available for the glass-maker, and it is accordingly used very extensively. It has the advantage of relative cheapness, and can be conveniently obtained and introduced into glass in the form of pure compounds whose colouring effect can be accurately anticipated; the colours produced by the aid of chromium have the further advantage of being very constant in character, being little affected by oxidising or reducing conditions, and only very slightly by the length or temperature of the melting process. The rate of cooling, in fact, appears to be the only factor that materially affects the colours produced by compounds of chromium. The colours produced by chromium alone are various depths of a bright green, the depth varying, of course, with the proportion of chromium that is present in the glass and with the purity of the glass itself. Very frequently chromium is used in conjunction with either iron or copper to produce various tints of "cold blue" and "celadon green" respectively. This element is most usually introduced into the glass mixture in the form of potassium bichromate; although other compounds might be employed, this substance presents several advantages to the glass-maker. In the first place, since the colouring effect of chromium is very intense, it must be used in very small quantities, and if chromic oxide itself were used, the weighing would have to be carried out with extreme care; potassium bichromate, however, contains a much smaller proportion

of the effective colouring substance, so that much larger weights can be employed, and the accuracy of weighing required is proportionately reduced. A further consideration arises from the fact that chromic oxide is itself an extremely refractory body, and is therefore comparatively difficult to incorporate with glass, while its presence tends to make the glass itself more viscid and refractory; the simultaneous introduction of the alkali, as provided by the use of the bichromate, is thus an advantage in restoring the fluidity and softness of the glass when finished, while also facilitating the solution of the chromium in the glass during the fusion process: this process of solution, however, takes some time, chromium glasses being liable to appear patchy if insufficient time is given to the "founding."

Uranium is one of the rarer and more costly elements, but is nevertheless used in glass-making for special purposes on account of the very beautiful fluorescent yellow colour which it imparts when added in small proportions. This yellow is quite characteristic and unmistakable, so that none of the other varieties of yellow glass can ever be used as a substitute for uranium glass, but the great cost of the latter prevents its extended use. Uranium is usually introduced into glass mixtures in the form of a chemical compound, such as uranyl-acetate or uranyl-nitrate, both these substances being obtainable in the form of small, intensely bright yellow crystals.

Fluorine occurs in a number of glasses in the form of dissolved or suspended fluorides, principally fluoride of aluminium. The element is not essentially a colouring substance, and is only mentioned here because the fluoride named is the most frequently used means of producing "opal" glass. The fluoride is most frequently introduced into the glass mixtures as calcium fluoride, used in conjunction with felspar, or as cryolite, a natural mineral which consists of a double fluoride of sodium and aluminium.

Manganese is one of the most important colouring elements used by the glass-maker. When introduced into glass in the absence of

other colouring ingredients, compounds of manganese produce a range of colours lying in the region of pinkish-purple to violet, according to the chemical nature of the glass. The exact colour produced varies according as the glass has lead, lime or barium as its base, and it also depends upon the presence of soda or potash as the alkaline constituent. The nature and intensity of the colour, however, which the addition of a given percentage of manganese will produce depends upon other factors besides the chemical composition of the bases used in the mixture. The heat and duration of the "found" and the reducing or oxidising conditions of the furnace in which it has been carried on very materially affect the result. Thus, a glass having a slight tinge of pink or purple derived from manganese can be rendered entirely colourless by the action of reducing gases or by introducing into the glass a reducing substance, such as a piece of wood. It will thus be seen that while manganese is a most useful element for the glass-maker, its employment requires much skill and care, and generally involves some troublesome manipulations before the desired result is attained.

In practice, manganese is most frequently used with other colouring ingredients for the production of what may be called "compound" colours, the function of the manganese being to provide the "warm" element, *i.e.*, the pink or purple component, required. One of the most important uses of manganese coming under this head is its use as a "decolouriser." By a "decolouriser" the glass-maker understands a substance which can be used to improve the colour of a glass which, from the nature of its raw materials and conditions of melting, would have a greener colour than is thought desirable for the product in question. It may be said at once that the most perfect and satisfactory method of obtaining the better colour required is to adopt the use of purer raw materials and methods of melting less liable to lead to contamination of the glass. On the other hand, this radical course is often impossible on the ground of expense, and the less satisfactory course must be adopted of covering one undesirable colour by another comple-

mentary colour which would, in itself, be equally undesirable. The rationale of this procedure depends upon the fact that a slight amount of absorption of light is not readily detected by the human eye if it be uniformly or nearly uniformly distributed over the whole range of the visible spectrum, *i.e.*, if the colour of the resulting light is nearly neutral, while an equally slight absorption in one region of the spectrum, while actually allowing more light to pass through the glass, is at once detected by the eye owing to the colour of the transmitted light. Now it has been found that the colour produced in glass by the addition of very small proportions of manganese is approximately complementary to the greenish-blue tinge of the less pure varieties of ordinary glass; the addition of manganese in suitable proportions to such glass therefore results in the production of a glass which transmits light of approximately neutral, usually slightly yellow, colour, the increased total absorption only becoming noticeable in large pieces. This "covering" of the greenish tinge is generally most completely successful in the case of soda-flint glasses, but the method is also used to a certain extent in the case of the soda-lime glasses used for sheet and plate-glass manufacture. Manganese added to glass for this purpose is generally introduced into the mixture in the form of the powdered black oxide (manganese dioxide), which is available as a natural ore in a condition of sufficient purity. Added in this form, the manganese compound exerts a double action, the decomposition of the dioxide resulting in the liberation of oxygen within the mass of melting glass, and this oxygen itself exerts a favourable influence on the resulting colour of the glass, since it removes organic materials whose subsequent reducing action would be deleterious, and it also converts all iron compounds present into the more highly-oxidised (ferric) state in which their colouring effects are less intense. The actual colouring effect of the manganese itself is, of course, afterwards developed, and produces the effects discussed above.

The "covering" of the greenish tints due to iron and other compounds is only possible when these are present in very small

proportions. When larger quantities of these substances have been introduced into the glass the addition of manganese modifies the resulting colour, but is no longer able to neutralise it. A very large range of colours can be obtained by using various proportions of iron and manganese, the best-known of these being the warm brown tint known as "hock-bottle," while all shades between this and the bright green of iron and the purple of manganese can be obtained by suitable mixtures. What has been said above as to the sensitiveness of manganese colours applies with even greater force to these mixed tints, since here both the iron and the manganese compounds are liable to undergo changes of oxidation. Copper-manganese and chromium-manganese colours are also used, as indeed almost any number of colouring ingredients may be simultaneously introduced into a glass mixture, the resulting colour being, as a rule, purely additive.

Iron is so widely distributed among the materials of the earth's crust that it is exceedingly difficult to exclude it entirely from any kind of glass, although the purest varieties of glass contain the merest traces of this element. Cheaper varieties of glass, however, always contain iron in measurable quantity, while the cheapest kinds of glass contain considerable proportions of this element. The colouring effects of iron have already been alluded to at various points in the earlier chapters as well as in the section on manganese just preceding. Little further remains to be said here. Just as the less highly oxidised compounds of iron—*i.e.*, the "ferrous" compounds—always show a decided green tint, so glasses containing iron when melted under the usually prevalent reducing conditions of a glass-making furnace, show a decided green tint whose depth depends upon the amount of iron present, provided no manganese or other "decolouriser" has been introduced. "Ferrous" compounds are, however, readily converted into the more highly oxidised or "ferric" state by the action of oxidising agents, and this change can also be brought about in molten glass by the action of such substances as nitrates or other sources of

oxygen. The ferric compounds, however, show characteristic yellow tints which are much less intense and vivid than the corresponding green colours of the "ferrous" series, and a similar result is brought about by the oxidation of iron compounds contained in glass; hence the "washing" or cleansing effects ascribed to oxidising agents introduced in the fusion of glass. It should, however, be borne in mind that the oxidation of other substances besides iron compounds, viz., organic matter, carbon and sulphur compounds, may, and probably does, play a most important part in this process in the case of most varieties of glass.

Nickel exerts a powerful colouring influence on glass, in accordance with the fact that most of the other compounds of this element are also deeply coloured. The exact colour produced in glass depends upon the nature of the glass and on the condition of oxidation in which the nickel is present. The colours, however, are usually of a greenish-brown tint, although brighter colours can be produced by nickel under special conditions. This element is not much used as a colouring agent in practice, although it has been advocated as a "decolouriser." The writer is not, however, aware that it has ever been successfully used for this purpose, and, in fact, the colours to which it gives rise do not appear to be even approximately complementary to the ordinary green and blue tints which "decolourisers" are intended to cover.

Cobalt is one of the most powerful colouring agents in glass, and is very largely used in the production of all varieties of blue glass. The blue colour produced by cobalt is, in fact, probably the most "certain" of the colours available to the glass-maker, this tint being least affected by all those circumstances that lead to variations in other tints. Almost the only difficulty involved in the use of cobalt is the great colouring power of this element, which requires that for most purposes only very small quantities may be added to the glass mixture. Formerly cobalt was added to glass mixtures in the form of "zaffre," which was a very impure form of cobalt oxide. At the present time, however, the more expensive but much

more satisfactory pure oxide of cobalt is in almost universal use. This substance shows a perfectly constant composition and, by means of accurate weighing, enables the glass-maker to introduce precisely the right amount of cobalt into his batch.

The range of colours which are available to the modern glass manufacturer are, as will be seen from a consideration of the list of colouring elements given above, practically unlimited, particularly as these substances can be used in almost any combination to produce mixed or intermediate tints. This practically infinite variety of possible tints, indeed, involves the principal difficulty encountered by the manufacturer of coloured glass, *i.e.*, that of matching his tints, or of keeping the colour of any particular variety of glass so constant that pieces produced at various times can be used indiscriminately together. This ideal is, perhaps, never entirely realised, but in the case of glasses intended for special technical uses the ideal degree of constancy is very closely approached.

In addition to being called upon to produce a large variety of different tints, the glass-maker is also called upon to produce various depths of the same tint. In many cases this can be readily done by the simple means of varying the amount of colouring material added to the glass. Where the colouring effect of small quantities of these substances is not excessively powerful there is no very great difficulty in doing this, but in certain cases this mode of regulating the intensity of the colour is not available. Thus copper-ruby glass cannot readily be made of so light a tint as to appear of reasonable depth when used in sheets of the thickness of ordinary sheet-glass. As has already been indicated, the desired tint is obtained by the process of "flashing," *i.e.*, of placing a very thin layer of deep ruby-coloured glass upon the surface of a sheet of ordinary more or less colourless glass of the usual thickness. This is generally accomplished by having a pot of molten ruby glass available close to a pot from which colourless glass is being gathered. A small gathering of ruby glass is first taken up on the pipe, and the remaining gatherings required for the production of the sheet are taken from the pot of

colourless glass. When such a composite gathering is blown into a cylinder in the manner described in the previous chapter, the ruby glass lies as a thin layer over the inner face of the cylinder, but special care and skill on the part of the gatherer and blower are required to ensure that this layer shall be evenly distributed and of the right thickness to produce just the tint of ruby required. Since the whole layer of red glass is so thin, a very slight want of uniformity in its distribution leads to wide variations of tint, and in practice these are often seen in the less successful cylinders of such glass.

The chemical composition of the ruby and the colourless glass which are to be employed for this purpose must also be properly adapted to one another in order to produce two glasses which shall have as nearly the same coefficient of thermal expansion as possible. If this requirement is not met, the resulting glass is subjected to internal strains which may lead to fracture, while, if the ruby glass has the higher co-efficient of expansion, the sheet after flattening tends to draw itself up on the " flashed " side and cannot be passed out of the annealing kiln in a properly flat condition.

Although most usually applied to copper-ruby glass, the flashing process is often used with other colours also. Coloured glass of this kind is at once recognised when looked at through the edges. Thus examined the glass simply shows the greenish tint of ordinary sheet-glass which constitutes practically the entire thickness of the sheet. In the same way, if such " flashed " glass be cut or etched in such a way that the layer of coloured glass is removed in places, the resulting pattern appears in white on the coloured ground—a feature which is utilised for certain decorative purposes. The flashing process just described, it should be noted, is applicable to any form of glassware which is blown from a gathering, and the coloured layer can be applied either upon the inside or outside of any object thus produced.

In addition to the palette of colours which the glass-maker is able to supply, the artist in stained glass has a further range of colours at his disposal in the form of stains and transparent colours which can be applied to the surface of glass and developed and rendered more

or less permanent by being properly "fired." The colours produced in this way are also, in one sense, coloured glasses, or rather glazes, whose raw materials are put upon the glass by the brush of the painter, and only subsequently caused to combine and melt by suitable heating. The degree of heat applicable under these circumstances is, however, very limited by the necessity of avoiding any great softening of the substratum of glass, while many of the colours themselves are composed of materials which could not resist very high temperatures. The fluxes used in the composition of these colours must for this reason be of a very fusible kind, with the inevitable result of a greatly reduced chemical stability as compared with the glass itself.

The whole subject of painting on glass, even from the purely technical as apart from the æsthetic point of view, is a very wide one, and lies outside the scope of the present volume. Only one further technical point in connection with glass-painting and stained glass work will therefore be touched upon here. This is an example of the fact that the more technically "perfect" modern product is not always preferable for special purposes which have been well served by older and far less "perfect" products. The production of technically excellent coloured glass in modern times was, somewhat surprisingly at first, accompanied by a very marked decline in the artistic beauty of stained glass windows produced with this modern material; the ancient art of stained glass was, therefore, for a time regarded as a "lost art," and glass-makers were blamed for being unable to produce the brilliant and beautiful tints which had been formerly available. More careful study, however, revealed the fact that while the actual colour of modern glass was at least as brilliant and varied as that of ancient glass, the difference lay in the fact that the modern glass was practically entirely free from such imperfections as air-bubbles, striæ, and other defects which improved appliances and methods had enabled the glass-maker to eliminate from his products. Finding the beauty of his wares greatly improved by this increased purity of the glass in the case of window glass and

table ware, it was natural for the glass-maker to endeavour to produce the same " improvement " in the coloured glasses intended for artistic purposes and, indeed, it is more than likely that the stained-glass workers themselves pressed this line of improvement upon him by a demand for " better " glass. It turned out, however, on close examination, that this very perfection of modern glass rendered it less adapted for these artistic purposes. A perfect piece of glass, having smooth surfaces and no internal irregularities, allows the rays of light falling upon it to pass through undeflected in direction, and merely changed in colour, according to the tint of the glass in question. On looking at the glass, external objects can be quite clearly seen, and much of the interest and mystery of the glass itself is lost. On the other hand, when falling upon a piece of glass having an irregular surface, and containing all manner of irregularities such as striæ, air bells, and even pieces of enclosed solid matter, the light is scattered, refracted, and deflected into all manner of directions until it almost appears to emanate from the body of the glass itself, which thus appears almost to shine with an internal light of its own ; the eye can hardly perceive the presence of external objects, and the whole window appears as a brilliant self-luminous object.

Once their attention had been drawn to these facts, modern glass-makers endeavoured, and with much success, to reproduce the desirable qualities of the ancient glass, while still availing themselves of modern methods to produce more stable glasses and a wider range of colours. The irregular surface of the old glass is imitated by using rolled or " muffed " instead of ordinary blown glass, while the internal texture is rendered non-homogeneous by the deliberate introduction of solid and gaseous impurities and by manipulations so arranged as to leave the glass in layers of different density, which appear in the finished glass as " striæ." As a consequence, it is probably not too much to claim that the modern workers in coloured glass have materials at their disposal which are at least as suitable for the purpose as those that were available in the best days of the ancient art.

Some reference has already been made to the technical uses of coloured glass, but one or two further points in that connection remain to be discussed. For such technical purposes as railway and marine signals, the consensus of practical experience has decided in favour of certain colours of glass, such as red and green of particular tints. On the other hand, for various purposes in connection with photography, the glass-maker does not appear to have been able to meet the new requirements, with the result that flimsy and otherwise unsatisfactory screens made of gelatine or celluloid stained with organic dyes are employed in place of coloured glass in such cases, for example, as the covering of lamps for use in photographers' "dark rooms," and for the light-filters used for orthochromatic and tri-chromatic photography. In all these cases it is necessary to use a transparent coloured medium which transmits only light of a certain very definite range of wave-lengths, and there is no doubt that for the glass-maker, who is confined to the use of a number of elementary bodies for his colouring media, it is by no means easy to comply with these requirements of exact transmission and absorption. On the other hand, the field of available coloured glasses has not been fully explored from this point of view, the only extensive work on the subject having been done in connection with the Jena firm of Schott, who have put upon the market a series of coloured glasses of accurately-known absorbing power. There is, however, little doubt that a much greater extension of this field is possible, and that it will be opened up by a glass-maker who undertakes the exhaustive study of coloured glasses from this point of view, although it must be admitted that there is considerable doubt whether the results obtainable by the aid of aniline and other dyes as applied to gelatine can ever be equalled by coloured glasses.

CHAPTER XIII

OPTICAL GLASS

Optical glass differs so widely from all other varieties of glass that its manufacture may almost be regarded as a separate industry, to which, indeed, a separate volume could well be devoted. In the present chapter we propose to give an outline of the most important properties of optical glass, and in the next chapter to describe the more important features of the processes used in its production.

The properties which affect the value of optical glass may roughly be divided into two groups. The first group comprises the specifically "optical" properties—*i.e.*, those directly influencing the behaviour of light in its passage through the glass, while the second group covers those properties of a more general nature, which are of special importance in glass that is to be used for optical purposes.

Optical Properties of Glass.—The most essential property of glass in this respect is homogeneity. We have already indicated that glass can never be regarded as a definite chemical substance or compound, but that it usually consists of mutual solutions of various complex silicates, borates, etc. Solutions being of the very nature of mixtures of two or more different substances, it follows that they can only become homogeneous when *complete* mixing has taken place. We have a familiar example of the formation of such a solution when sugar is dissolved in water. The water near the sugar becomes saturated with sugar and of different density from the remaining water; if the liquid is *slightly* stirred a very characteristic phenomenon makes its appearance—the pure water and the dense sugar solution do not at once mix completely, the denser liquid remaining for a time disseminated throughout the whole

fluid mass in the form of more or less fine lines, sheets, or eddies, and these are visible because the imperfectly mixed liquids have different effects on the light passing through them. In the case of sugar-water we are, however, dealing with a very mobile liquid, and a few turns of a tea-spoon suffice to render the mixture complete, and the liquid, which for a few moments had appeared turbid, becomes homogeneous and transparent. In the case of glass, when the raw materials are melted together, a mixture is formed of liquids of differing densities similar to that which was temporarily formed in the sugar-water solution. Molten glass, however, is never so mobile a liquid as ordinary water, nor is it in the ordinary course of manufacture subjected to any such thorough mixing action as that which is produced by a spoon in a glass of water. In glass as ordinarily manufactured, therefore, it is not surprising to find that the lack of homogeneity which originates during the melting persists to the end. Its effects can be traced whenever a thick piece of ordinary glass is carefully examined, when the threads or layers of differing densities can be recognised in the form of minute internal irregularities in the glass. These defects are known as striæ or veins, and their presence in glass intended for the better kind of optical work renders the glass useless. As will be seen below, in the production of optical glass special means are adopted for the purpose of rendering it as homogeneous as possible; in fact, the early history of optical glass manufacture is simply the history of attempts to overcome this very defect. The problem is, however, beset by chemical and physical difficulties of no mean order, and even in the best modern practice only a small proportion of each melting or crucible full of glass is entirely free from veins or striæ. In many cases these defects are very minute, and sometimes escape observation until the stage of the finished lens is reached. At that stage, however, their presence becomes painfully evident from the fact that they interfere seriously with the sharp definition of the images formed by the lens in question. It will be seen that in such a case time and money has been wasted by grinding and polishing

what turns out to be a useless piece of glass. Methods are, therefore, used for examining the glass before it is worked, whereby the existence of the smallest striæ can scarcely escape detection. These methods depend upon the principle that a beam of parallel light passing through a plate of glass will meet with no disturbance so long as the glass is homogeneous, but if striæ are present, they will cause the light to deviate from parallelism wherever it falls upon them. Under such illumination, therefore, the striæ will appear as either dark or bright lines, when they can be readily detected. One form of apparatus used for this purpose is illustrated in Fig. 16.

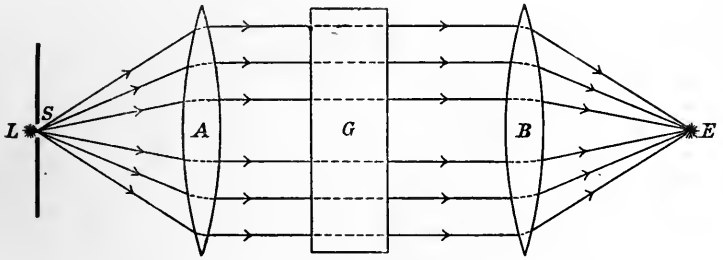

FIG. 16.—Diagram of striæ-testing apparatus.

L, source of light; *S*, slit; *A* and *B*, simple convex lenses; *G*, glass under test; *E*, eye of observer. The arrows indicate the path of light-rays.

Transparency and *colour* are obviously fundamentally important properties of glass. In one sense homogeneity is essential to transparency, but the aspect of the subject which we are now considering is that of the absorption of light in the course of regular transmission through glass. It may be said at once that no glass is either perfectly transparent or, what comes to nearly the same thing, perfectly free from colour. In the case of the best optical glasses it is true that the absorption of light is very slight, but even these, when considerable thicknesses are viewed, show a greenish-yellow or bluish colouring. On the other hand, certain optical glasses which are used at the present time for many of our best lenses absorb light so strongly or are so deeply coloured that a thickness of a few

inches is sufficient to reveal this defect. To some extent public taste or opinion which objects to the use of even a slightly *greenish* glass in optical instruments of good quality is to blame for the tint of these glasses. In many cases glass-makers could produce a very slightly greenish glass, but in order to overcome this colour they deliberately add to the glass a colouring oxide imparting a colour more or less complementary to the natural green tint. The result is a more or less neutral-tinted glass which, however, absorbs much more light than the naturally green glass would have done. Since such glass is frequently used for photographic lenses, it is interesting to note that the light rays whose transmission is sacrificed in order to avoid the green tint are those lying at or near the blue end of the spectrum, so that the photographic rapidity of the resulting lenses is decidedly reduced by the use of such glass.

Refraction and Dispersion.—The quantitative properties of glass, governing its effect upon incident and transmitted light, are, of course, of fundamental importance in all its optical uses. The fundamental optical constant of each variety of optical glass is known as its refractive index; this number really represents the ratio of the velocity with which light waves are propagated through free space to the velocity with which they travel through the glass. Not only does this ratio vary with every change in the chemical composition and physical condition of the glass, but it also varies according to the length of the light waves themselves. In other words, the short waves of blue light are transmitted through glass more slowly than the longer waves of red light. The consequence is that when a beam of white light is passed through a prism it is split up and spread out into a number of beams representing all the colours of the spectrum in their proper order, the blue light suffering the greatest deflection from its original path, while the red light suffers least deflection. Both the actual and relative amount by which light rays of various colours are deflected under such circumstances depends upon the nature of the glass in question; therefore, fully to characterise the optical pro-

perties of a given kind of glass it is necessary to state not only its refractive index but to specify the refractive indices for a sufficient number of different wave-lengths of light, suitably distributed through the spectrum. For this purpose a number of well-marked spectrum lines have been chosen. Fraunhofer first used the dark lines in the solar spectrum (A to H) for this purpose, but Abbé substituted for these a series of lines which can be produced at will in the laboratory. The actual lines chosen are the line known as A′, corresponding to a wave-length of 0·7677 micro-millimetres and the lines known as C, D, F, and G′, whose wave-lengths, in the same units, are 0·6563, 0·5893, 0·4862, and 0·4341 respectively. The A′ line, however, lies so near the extreme red end of the spectrum that the data concerning it are seldom required.

As a matter of fact, the actual refractive index is only stated in most tables of optical glasses for sodium light (D line), the dispersive properties of the glass being indicated by tabulating the differences between the refractive indices for the various lines, the table thus containing columns marked C-D, D-F, F-G′. These figures are usually described as the "dispersion" of the glass from C to D, D to F, etc. In addition to these figures it is usual to tabulate what is called the "mean dispersion" of the glass, which is simply the difference between the refractive indices for C and F lines; this interval is usually taken as representing that part of the spectrum which is of the greatest importance for visual purposes. A further constant which is of great importance in the calculations for achromatic lenses is obtained by dividing the mean dispersion into the refractive index for the D line minus one (usually written $\frac{C-F}{n_D-1}=\nu$).

This term, for which no satisfactory name has yet been suggested, characterises the ratio of the dispersive power of the glass to its total refracting power. It is usually denoted by the Greek letter ν. The following tables give lists of optical glasses produced by Messrs. Chance, of Birmingham. This list contains examples of all the

TABLE OF OPTICAL GLASSES.—I.

Arranged in the order of the values of ν.

Name.	n_D	Dispersion C – F.	ν.	Partial Dispersions.		
				C – D.	D – F.	F – G'.
Fluor Crown	1·4783	·00671	71·3	·00201	·00470	·00370
Fluor Crown	1·4785	·00682	70·2	·00202	·00480	·00363
Boro-Silicate Crown	1·5087	·00793	64·2	·00237	·00556	·00448
Boro-Silicate Crown	1·5160	·00809	63·8	·00240	·00569	·00453
Boro-Silicate Crown	1·5194	·00825	62·9	·00243	·00582	·00465
Boro-Silicate Crown	1·5126	·00818	62·7	·00241	·00577	·00458
Dense Barium Crown	1·5881	·00962	61·1	·00284	·00678	·00544
Hard Crown	1·5155	·00848	60·8	·00249	·00599	·00485
Hard Crown	1·5175	·00856	60·5	·00252	·00604	·00484
Hard Crown	1·5186	·00860	60·3	·00252	·00608	·00491
Hard Crown	1·5204	·00869	59·9	·00255	·00614	·00492
Light Barium Crown	1·5407	·00910	59·4	·00267	·00643	·00517
Hard Crown	1·5215	·00878	59·4	·00258	·00620	·00497
Hard Crown	1·5193	·00877	59·2	·00259	·00620	·00497
Dense Barium Crown	1·5995	·01017	59·0	·00299	·00718	·00578
Dense Barium Crown	1·5938	·01006	59·0	·00299	·00707	·00570
Dense Barium Crown	1·6118	·01037	59·0	·00304	·00733	·00590
Dense Barium Crown	1·5981	·01019	58·7	·00300	·00719	·00580
Dense Barium Crown	1·6065	·01046	57·9	·00308	·00738	·00589
Zinc Crown	1·5149	·00890	57·9	·00265	·00625	·00502
Medium Barium Crown	1·5708	·00986	57·9	·00290	·00696	·00563
Medium Barium Crown	1·5744	·00995	57·9	·00291	·00704	·00570
Soft Crown	1·5152	·00906	56·9	·00264	·00642	·00517
Dense Barium Crown	1·6140	·01080	56·9	·00316	·00764	·00618
Dense Barium Crown	1·6114	·01077	56·8	·00315	·00762	·00616
Dense Barium Crown	1·6126	·01080	56·7	·00316	·00764	·00617
Dense Barium Crown	1·6151	·01089	56·5	·00319	·00770	·00621

Dense Barium Crown	1·6066	·01076	56·4	·00314	·00762	·00618
Medium Barium Crown	1·5660	·01006	56·3	·00297	·00709	·00576
Dense Barium Crown	1·6084	·01085	56·1	·00318	·00767	·00620
Medium Barium Crown	1·5837	·01041	56·1	·00304	·00737	·00598
Dense Barium Crown	1·6065	·01090	55·6	·00320	·00770	·00619
Baryta Light Flint	1·5670	·01032	54·9	·00302	·00730	·00593
Light Barium Flint	1·5452	·01020	53·5	·00298	·00722	·00582
Extra Light Flint	1·5250	·01016	51·7	·00298	·00718	·00582
Light Barium Flint	1·5515	·01067	51·7	·00308	·00759	·00623
Extra Light Flint	1·5290	·01026	51·6	·00300	·00726	·00596
Light Barium Flint	1·5523	·01075	51·4	·00311	·00764	·00620
Extra Light Flint	1·5316	·01085	49·0	·00313	·00772	·00630
Extra Light Flint	1·5333	·01099	48·5	·00322	·00777	·00640
Light Flint	1·5412	·01136	47·6	·00328	·00808	·00668
Light Barium Flint	1·5833	·01251	46·6	·00362	·00889	·00721
Light Barium Flint	1·5534	·01201	46·1	·00345	·00856	·00711
Light Flint	1·5472	·01196	45·8	·00348	·00848	·00707
Light Flint	1·5491	·01206	45·5	·00348	·00858	·00714
Baryta Light Flint	1·5734	·01299	44·1	·00374	·00925	·00769
Baryta Light Flint	1·5760	·01331	43·3	·00383	·00948	·00794
Light Flint	1·5610	·01299	43·2	·00372	·00927	·00707
Light Flint	1·5632	·01312	42·9	·00375	·00937	·00784
Light Flint	1·5746	·01388	41·4	·00396	·00992	·00830
Light Flint	1·5760	·01404	41·0	·00402	·01002	·00840
Light Flint	1·5787	·01420	40·7	·00404	·01016	·00840
Dense Flint	1·6041	·01599	37·8	·00455	·01144	·00961
Dense Flint	1·6089	·01632	37·3	·00468	·01164	·00986
Dense Flint	1·6125	·01655	37·0	·00469	·01186	·01003
Dense Flint	1·6134	·01662	36·9	·00471	·01191	·01008
Dense Flint	1·6118	·01657	36·9	·00470	·01187	·01004
Dense Flint	1·6182	·01697	36·4	·00484	·01213	·01026
Dense Flint	1·6214	·01722	36·1	·00491	·01231	·01046
Dense Flint	1·6225	·01729	36·0	·00493	·01236	·01054
Extra Dense Flint	1·6469	·01917	33·7	·00541	·01376	·01170
Extra Dense Flint	1·6501	·01936	33·6	·00544	·01392	·01190
Double Extra Dense Flint	1·7129	·02384	29·9	·00670	·01714	·01661
Double Extra Dense Flint	1·7566	·02754	27·5	·00774	·01980	·01736

TABLE OF OPTICAL GLASSES.—II.

Arranged in the order of the values of n_D.

Name.	n_D	Dispersion C – F.	ν.	Partial Dispersions.		
				C – D.	D – F.	F – G'.
Fluor Crown	1·4783	·00671	71·3	·00201	·00470	·00370
Fluor Crown	1·4785	·00682	70·2	·00202	·00480	·00363
Boro-Silicate Crown	1·5087	·00793	64·2	·00237	·00556	·00448
Boro-Silicate Crown	1·5126	·00818	62·7	·00241	·00577	·00458
Zinc Crown	1·5149	·00890	57·9	·00265	·00625	·00502
Soft Crown	1·5152	·00906	56·9	·00264	·00642	·00517
Hard Crown	1·5155	·00848	60·8	·00249	·00599	·00485
Boro-Silicate Crown	1·5160	·00809	63·8	·00240	·00569	·00453
Hard Crown	1·5175	·00856	60·5	·00252	·00604	·00484
Hard Crown	1·5186	·00860	60·3	·00252	·00608	·00491
Hard Crown	1·5193	·00877	59·2	·00259	·00620	·00497
Boro-Silicate Crown	1·5194	·00825	62·9	·00243	·00582	·00465
Hard Crown	1·5204	·00869	59·9	·00255	·00614	·00492
Hard Crown	1·5215	·00878	59·4	·00258	·00620	·00497
Extra Light Flint	1·5250	·01016	51·7	·00298	·00718	·00582
Extra Light Flint	1·5290	·01026	51·6	·00300	·00726	·00596
Extra Light Flint	1·5316	·01085	49·0	·00313	·00772	·00630
Extra Light Flint	1·5333	·01099	48·5	·00322	·00777	·00640
Light Barium Crown	1·5407	·00910	59·4	·00267	·00643	·00517
Light Flint	1·5412	·01136	47·6	·00328	·00808	·00668
Light Barium Flint	1·5452	·01020	53·5	·00298	·00722	·00582
Light Flint	1·5472	·01196	45·8	·00348	·00848	·00707
Light Flint	1·5491	·01206	45·5	·00348	·00858	·00714
Light Barium Flint	1·5515	·01067	51·7	·00308	·00759	·00623
Light Barium Flint	1·5523	·01075	51·4	·00311	·00764	·00620
Light Barium Flint	1·5534	·01201	46·1	·00345	·00856	·00711
Light Flint	1·5610	·01299	43·2	·00372	·00927	·00707

Light Flint	1·5632	·01312	42·9	·00375	·00937	·00784
Medium Barium Crown	1·5660	·01006	56·3	·00297	·00709	·00576
Baryta Light Flint	1·5670	·01032	54·9	·00302	·00730	·00593
Medium Barium Crown	1·5708	·00986	57·9	·00290	·00696	·00563
Baryta Light Flint	1·5734	·01299	44·1	·00374	·00925	·00769
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Dense Barium Crown	1·5981	·01019	58·7	·00300	·00719	·00580
Dense Barium Crown	1·5995	·01017	59·0	·00299	·00718	·00578
Dense Flint	1·6041	·01599	37·8	·00455	·01144	·00961
Dense Barium Crown	1·6065	·01090	55·6	·00320	·00770	·00619
Dense Barium Crown	1·6065	·01046	57·9	·00308	·00738	·00589
Dense Barium Crown	1·6066	·01076	56·4	·00314	·00762	·00618
Dense Barium Crown	1·6084	·01085	56·1	·00318	·00767	·00620
Dense Flint	1·6089	·01632	37·3	·00468	·01164	·00986
Dense Barium Crown	1·6114	·01077	56·8	·00315	·00762	·00616
Dense Barium Crown	1·6118	·01037	59·0	·00304	·00733	·00590
Dense Flint	1·6118	·01657	36·9	·00470	·01187	·01004
Dense Flint	1·6125	·01655	37·0	·00469	·01186	·01003
Dense Barium Crown	1·6126	·01080	56·7	·00316	·00764	·00617
Dense Flint	1·6134	·01662	36·9	·00471	·01191	·01008
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Dense Flint	1·6214	·01722	36·1	·00491	·01231	·01046
Dense Flint	1·6225	·01729	36·0	·00493	·01236	·01054
Extra Dense Flint	1·6469	·01917	33·7	·00541	·01376	·01170
Extra Dense Flint	1·6501	·01936	33·6	·00544	·01392	·01190
Double Extra Dense Flint	1·7129	·02384	29·9	·00670	·01714	·01661
Double Extra Dense Flint	1·7566	·02754	27·5	·00774	·01980	·01736

most important types of optical glass which are available at the present time. Those, however, who wish to use the data for the purpose of lens calculation are advised to consult the latest issues of the optical glass-makers' catalogues, since the range of types available, and even the actual figures for some of the glasses, are liable to variation from time to time.

In the tables on pp. 202—205 the first column contains the ordinary trade name by which each type of glass is known. These names, while somewhat arbitrary, indicate in a rough way the chemical nature of the glass concerned. Thus the word "flint" always implies a glass containing lead and therefore having a comparatively high refractive index and low value of ν, while the word "crown," originally applied only to lime-silicate glasses, is now used for all glass having a high value of ν. In the next column of the table are given the refractive indices of the glasses, while the fourth column contains the values of ν. It will be seen that in the first table the glasses are arranged in descending order of magnitude in respect of this constant. An inspection of the figures in these two columns will reveal the fact that for the majority of the glasses contained in this table the value of ν decreases as the refractive index increases. As a matter of fact this rule applied to practically all glasses that were known or were at all events commercially available prior to the modern advances in optical glass manufacture which were initiated by Abbé and Schott of Jena. It was Abbé's insight into the requirements of optical instrument design that led him to realise the importance of overcoming this limitation in the ratio between the dispersive and refractive powers of glass. With the collaboration of Schott he succeeded in producing a whole series of previously unknown varieties of optical glass in which the relation between n_D and ν is not that of approximately simple inverse proportionality which holds for the older crown and flint glasses. Most valuable and in many ways most typical of these new glasses are those known as the "barium crown" glasses, which combine the

high refractive index of a light flint or even a dense flint glass with the high ν value of an ordinary crown glass. The second table, in which the glasses are arranged in the order of their refractive indices, serves to show how far it has been possible to modify the dispersion for a given value of the refractive index. It would lead too far into the subject of lens construction to explain in detail the possibilities opened up to the optician by the use of these newer varieties of glass. We must content ourselves with pointing out that the great forward strides marked by the production of apochromatic microscope objectives, of anastigmatic photographic lenses, and the modern telescopes are all based upon the employment of these new optical media; and although optical glasses of these newer types are at the present time produced in the optical glass manufactories of France and England, in quality and quantity at least equal to the output of the Jena works themselves, these great optical achievements stand as a lasting monument to the pioneer work of Abbé and Schott in this field.

The last six columns of the table of optical glasses given above contain figures which define the manner in which each of the glasses named distributes the various sections of the spectrum. The columns C-D, D-F, and F-G′ give, as already indicated, the differences between the refractive indices for the C, D, F and G′ lines respectively; these differences, divided by the mean dispersion of the glass (C — F′) give the quantities known as the relative partial dispersions. If all kinds of glass distributed the various portions of the spectrum in the same proportionate manner, merely differing in the total amount of dispersion produced, these figures would be identically the same for all glasses. In actual fact it will be seen that the figures differ very widely from one type of glass to another. A moment's consideration will show that when two glasses are used in a lens for the purpose of achromatising one another, *i.e.*, when one is used to neutralise the dispersion of the other, such achromatisation can only be perfect if these ratios (the relative partial dispersions) are the same for both glasses. To put the same statement in more

concrete terms, if the spectrum produced by one glass is comparatively long drawn out at the red end, and relatively compressed at the blue end, while in the other glass the opposite relation holds between the two ends of the dispersion spectrum, it is evident that the two spectra can never be superposed in such a way as entirely to neutralise one another—the spectrum produced by the one glass will predominate and leave a residual colour at the blue end, while the other will predominate at the other end. In the case of lenses achromatised by the use of such glasses, there will always be a slight fringe of colour around the borders of the images which they produce. One of the aims which Abbé and Schott set themselves in the production of new varieties of optical glass was to obtain one or more pairs of glasses in which the relative partial dispersions should be as nearly alike as possible while the actual values of ν should differ as widely as possible. Some success in this direction was at first claimed by the Jena workers, but unfortunately some of the most promising glasses in this respect were found to be too unstable for practical use and had ultimately to be abandoned. The only pair of glasses approximating to perfect achromatism offered by the Jena firm is that tabulated below, and it will be seen that although the relative partial dispersions are very closely alike, the ν values of the two glasses only differ by 10, and at least one of

Name.	n_D	ν	C − F.	C − D.	$\frac{c-d}{c-f}$	D − F.	$\frac{d-f}{c-f}$	F − G′.	$\frac{f-g'}{c-f}$
Telescope Crown .	1·5254	61·7	·00852	·00250	·292	·00602	·707	·00484	·568
Telescope Flint . .	1·5211	51·8	·001007	·00297	·294	·00710	·705	·00577	·573

these glasses is not readily obtainable in really satisfactory optical quality. On the other hand, by a suitable selection of *three* glasses, Cooke, of York, and other makers have been able to produce perfectly achromatised telescope objectives, which are usually termed "apochromatic." The problem has been solved for microscope objectives by Zeiss, of Jena, who have employed suitable glasses

in conjunction with the natural mineral fluorite and other crystals. From the glass-maker's point of view, however, the problem of producing a satisfactory pair of glasses capable of entirely achromatising one another has yet to be solved.

The table of optical glasses given above, although brief as compared with the lists issued by French and German optical glass-makers, fairly covers the range of practically available glasses, and a rapid inspection will at once show how extremely limited this range really is. Thus the refractive index varies only between the limits 1·47 and 1·71, and even if we admit as practical glasses such extreme types—offered by some makers—as would extend this range to 1·40 in one direction and to 1·80 in the other, this does not affect the present argument. Of course, a glass of a refractive index as low as 1·0, or even 1·10, is not theoretically possible, since the mere density of any substance enters into the factors that affect its refractive index, and a glass having a density lower than that of water (whose refractive index is about 1·3) is scarcely conceivable. In the other direction, however, the limits met with in the case of glass are considerably exceeded by certain natural mineral substances. Thus the diamond has a refractive index of 2·42, while the garnets show refractive indices from 1·75 to 1·81. The values of ν found in the table of optical glasses are still more narrowly restricted, lying between 67 and 29, while such a mineral as fluorite shows a value of 95·4. These facts show that it is physically possible to obtain transparent substances having optical properties lying far beyond the limited range covered by our present optical glasses, and it scarcely needs showing that if such an extended range of materials were available greatly increased possibilities would be opened up to the designer of optical instruments. It is consequently interesting to inquire as to the actual causes which limit the range of optical glasses at present available. It will be found that these limits are set by the properties of glass itself. While the more ordinary kinds of glass, having average optical properties and showing dispersive powers roughly conforming to the law of

inverse proportionality with refractive index which governs the older varieties of optical glass, are chemically stable substances, showing little tendency to undergo either chemical changes or to crystallise during cooling, the more extreme glasses exhibit these undesirable features to an increasing extent the more nearly the limit of our present range is approached. As the chemical composition of a glass is "forced" by the addition of special substances intended to affect its optical properties in an abnormal direction, so the chemical and physical stability of the glass is rapidly lessened. The more extreme glasses, in fact, behave as active chemical agents readily entering into reaction or combination even with relatively inert substances in their environment—they act vigorously upon the fire-clay vessels in which they are melted, and they are readily attacked by acids, moisture or even warm air, when in the finished condition, while many of them can only be prevented from assuming the condition of a crystalline (and opaque) agglomerate by being rapidly cooled through certain critical ranges of temperature. A limit to the possibility of production is set by these tendencies when they exceed a certain amount—a point being reached where it ceases to be practicable to overcome the tendency of the glass to self-destruction. On the lines of our present glasses, therefore, it does not appear hopeful to look for any considerable extension of the range of our optical media. On the other hand, as the known optical properties of transparent crystalline minerals show, a much greater range of optical constants would become available if it were possible to manufacture artificial mineral *crystals* of sufficient size and purity for optical purposes, and the author believes that in this direction progress in optical materials is ultimately bound to lie.[1]

In addition to possessing the requisite optical constants, a good colour and perfect homogeneity, certain other properties are essential

[1] See a Paper by the present author on "Possible Directions of Progress in Optical Glass"—Proceedings of the Optical Convention. London. 1905.

in good optical glass. These are the general physical and chemical qualities which are essential in all good glass, but especially emphasised by the fact that the requirements for optical glass are more stringent than for any other variety of the material. Thus chemical stability is of the greatest importance, for the best lenses would soon become useless if the action of atmospheric moisture were to affect them appreciably—the polished surfaces would rapidly become dull and the whole lens would soon be rendered useless. The conditions governing the chemical stability of glass and the methods of testing this quality have already been indicated (Chapters I. and II.). The harder varieties of optical glass, such as the glasses quoted in the tables pp. 202–205 under the names of "Hard Crown" and "Boro-Silicate Crown," are probably among the most durable and chemically resistant of all varieties of glass, but as we have already indicated, when extreme optical properties are required, the necessary chemical composition of the glass always entails a sacrifice of this great chemical stability, until a limit is reached where valuable optical properties no longer counterbalance the serious disadvantage of a chemical composition which renders the glass liable to rapid disintegration.

In certain special cases it is, perhaps, possible to protect lenses made of such unstable glass by covering them with cemented-on lenses of stable glass, but this device entails concomitant limitations in the design of the optical system and is, therefore, rarely used. In any case, however, it is well for the lens-designer to consider the relative stability of the glasses employed when arranging the order in which they are to be used, since it is obviously preferable to put a hard, durable glass on the outside of his system, where it is most directly exposed to atmospheric moisture, and is also subject to handling and "cleaning" by inexpert hands. This latter factor is a very important one for the life of any lens. In the first place, a glass surface is very seriously affected by the minute film of organic matter which is left upon it when it has been touched with even a clean finger; unless the glass is of the best quality in this respect,

such finger-marks readily develop into iridescent spots and may even turn into black stains. Particles of dust allowed to settle on the surface of the glass will affect it in the same way, so that the protection afforded by mere mechanical enclosure in the tube of an instrument is of decided value in preserving a glass surface. It should, however, be noted that in some instances the interior metal surfaces of optical instruments are varnished with substances that give off vapours for a long time after the instrument is completed, and in that case the inside lenses are apt to be tarnished in consequence. On the other hand, outside lenses are also exposed to direct mechanical injury from handling and "cleaning." As far as the latter operation is concerned, it frequently happens, particularly in glasses containing soda, that a slight surface dimming is formed on the glass when it has been left in a more or less damp place for a long time. This dimming is chiefly due to the formation on the surface of a great number of very minute crystals of carbonate of soda, which are hard and sharp enough to scratch the glass itself if rubbed about over it. If such a lens be wiped with a dry cloth, however clean and soft, the effect is a permanent injury to the polished surface, which could readily be avoided by first washing the lens with clean water, or even by using a wet cloth instead of a dry one for the first wiping. The methods of testing glass for durability of surface have been described in Chapter I.

The mechanical hardness of the glass is an important factor in determining its resistance to such injurious treatment or to the effects of accidental contact with hard, sharp bodies. The subject of the hardness of glass has already been discussed in a general way in Chapter II., and little remains to be added here. Broadly speaking, a high degree of hardness and a low refractive index are found together. This statement is certainly true where any considerable difference of hardness is considered, as, for example, in comparing a hard crown glass with a dense flint; but where the difference of refractive index or of density is small, it is not at all certain that the lighter glass will also be the harder.

The properties involved in the quality known as " hardness " also affect in a very marked manner the behaviour of glass when subjected to the grinding and polishing processes. The ease with which a good polish can be obtained varies very much in different kinds of glass, both the hardest and the softest glasses showing themselves difficult in this respect. The harder glasses are certainly less liable to accidental scratching during the polishing operations, and generally work in a cleaner manner ; but the time required to produce a satisfactory polish is much greater owing to the resistance to displacement offered by the molecules. Both the speed of working and the pressure exerted during the polishing operation have, in fact, to be carefully adapted to the quality of the glass in this respect if the best possible results are to be obtained.

Another property which is essential in optical glass of the highest quality is that of freedom from internal strains. This subject will be again referred to later in connection with the annealing processes used in the manufacture of optical glass, and it need only be mentioned here that the presence of internal strain is readily recognised in glass, by the aid of the polariscope. Perfectly annealed glass, entirely free from internal strains, produces no effect upon a beam of polarised light passing through it, while even slightly strained glass becomes markedly doubly-refracting. For many purposes of optics this double refraction becomes undesirable or even inadmissible, especially as it is accompanied by small variations in the effective index of refraction of various portions of the mass of glass. Further, if the amount of double refraction observed is at all serious it indicates a state of strain which may easily lead to the fracture of the whole piece, particularly when undergoing the earlier stages of the grinding process or if exposed to shocks of any sort. As will be seen below, perfectly annealed glass is obtainable, but very special means are required for its production, and the optician should for that reason avoid making unnecessarily extreme demands in this direction. The very *small* amount of double refraction frequently found in the better class of optical glass is entirely harmless for most purposes.

CHAPTER XIV

OPTICAL GLASS

The process of manufacturing the best qualities of optical glass may be briefly described as consisting in obtaining a crucible full of the purest and most homogeneous glass, and then allowing it to cool slowly and to solidify *in situ*. From the resulting mass of glass the best pieces are picked and moulded into the desired shape for optical use. It will be seen at once that in this process there is an essential difference from all others that have been described in this book—viz., that the glass is never removed from the melting-pot while molten, and that none of the operations of gathering, pouring, rolling, pressing, or blowing are applied to it. The reason for this apparently irrational mode of procedure lies in the fact that the perfect homogeneity essential for optical purposes can only be attained by laborious means, and can then only be retained if the glass is left to solidify undisturbed; any movement by the introduction of pipes or ladles would result in the contamination of the glass by striæ and other objectionable defects.

The choice and proportion of raw materials used in the production of any given quality of optical glass is governed by the chemical composition which experiment has shown to be necessary to yield the desired optical properties. The composition of optical glass mixtures cannot therefore be varied to suit the conditions of the furnace or to facilitate ready melting and fining, so that many of the usual resources of the glass-maker cease to be available in the very case where their aid would be most welcome to facilitate the production of technically perfect glass. On the other hand, the manufacturer has a certain amount of choice as to the precise form in which

the various chemical ingredients are to be introduced into the mixture, and he makes his choice among oxides, carbonates, nitrates, and hydrates, according to the behaviour that it is desired to impart to the mass during the earlier stages of fusion. The state of purity in which the various substances are commercially obtainable also enters largely into the question, since the greatest possible degree of purity in the raw materials is essential to the production of glass of good colour, or rather freedom from colour. The extreme importance of purity of raw materials for optical glass is now so fully recognised that some manufacturers go to the length of carrying out a special purification process of certain of the chemicals, although these have been purchased as "pure."

Since homogeneity is so essential in the finished product, very thorough mixing of the raw materials is necessary in the case of optical glass, and the ingredients are for this purpose generally used in a state of finer division than is necessary with other varieties of glass. As a rule the quantities of mixture of any one kind that are required are not large enough to justify the use of mechanical appliances, and very careful hand-mixing is carried out.

Although it is quite possible to obtain successful meltings from raw materials alone, it is preferable to mix with these a certain proportion of "cullet" or broken glass derived from a previous melting of the same sort. The broken glass used for this purpose is first carefully picked over for the purpose of rejecting pieces that contain visible impurities, although pieces showing striæ are not usually rejected. The greater part of this cullet is generally mixed as evenly as possible with the raw materials, but a certain proportion is reserved for another purpose, as explained below.

The furnaces used for the production of optical glass vary very much in type. Until a few years ago some of the old conical coal furnaces were still in use. In these the pot stands on a block or "siege" raised between two very deep and wide grates; the whole space is domed over by a fire-brick dome through which apertures are pierced at intervals so as to allow the products of combustion

to pass out into the conical chimney which is built over the whole structure. These furnaces were very uneconomical, both because they could only obtain the desired high temperature by the use of picked coal in large quantities and also because so large a proportion of the heat escaped in the waste gases. There was the further disadvantage that the grates required clearing at intervals, and at those times the temperature of the furnace was liable to drop dangerously. These furnaces were, however, so cheap and simple in construction and their use was so deeply rooted in tradition that they have—in some works—only recently been superseded by much more efficient regenerative gas-fired furnaces. As a rule, however, optical glass furnaces differ from other pot-furnaces found in glass works in this respect—that the former are usually constructed to receive one or two pots or crucibles only, while in other glass furnaces from four to twelve or even twenty pots are heated at the same time. The reason for this restriction in the capacity of the furnaces lies in the fact that since the mixtures used for optical glass cannot be adjusted to suit the furnace, the latter must be worked as far as possible in such a way as to suit the mixture to be melted in it, and this implies that every pot will require its own adjustment of times and temperatures, and this it would be difficult, if not impossible, to secure if more than one or two pots were heated in the same furnace. It is further to be remembered that the amount of care and attention required during the melting of a pot of optical glass is out of all proportion to that needed with other varieties, so that little would be gained by having a number of pots in one furnace, since several sets of men would be required to tend them.

In addition to the melting furnace, a very important part of the equipment of the optical glass works is formed by a number of kilns which are used for the preliminary heating, and sometimes for the final cooling of the various crucibles or pots. Similar kilns are used in other branches of the industry, but in those cases the pots, once introduced into the furnace, are expected to last for a number of weeks, or even months. In optical glass manufacture, on the other

hand, a pot is used once only, so that fresh pots are required for every new melting. The kilns in which these pots are heated up before being placed in the melting furnace are thus in very frequent use. As a rule they are simply fire-brick chambers provided with sufficient grate-room and flue-space to be gradually raised to a red heat in the course of four or five days, while for the purpose of gradual cooling they can be sealed up like the annealing kilns used for polished plate-glass. In the most modern practice, however, a more elaborate type of kiln or "pot arch" is employed, as it has been recognised that it is desirable, in order to confer greater resisting power upon the pot, to give it a much higher degree of preliminary firing. While the older, simple coal-fired pot arches could barely attain a temperature of 1,000° C. the newer gas-fired pre-heating furnaces are so designed as to allow of the firing of the pot being carried as high as 1,400° C. Even then it is sometimes thought desirable, after the pre-heated pot has been "set" in the furnace, to carry the preliminary firing still further in the melting-furnace before any glass is charged into the pot. In that case the pre-firing is sometimes carried up to temperatures near 1,600° C., but in that case care is required to avoid attaining a temperature high enough to soften the pot and cause it to deform under its own weight. There can be no doubt, however, that such a preliminary hard firing of the pot is an undoubted advantage especially if a particularly highly refractory clay is used, as such clay is too porous if not adequately burnt.

The pots or crucibles in which optical glass is melted are usually of the same shape as the covered pots used for flint glass as illustrated in Fig. 2. The optical glass pots, however, are made considerably thinner in the wall, since they are not required to withstand the prolonged action of molten glass in the same way as pots used for flint glass manufacture. On the other hand, the fire-clays used for this purpose must be chosen with special care so as to avoid any contamination of the glass by iron or other impurities which might reach the glass from the pot. For the production of certain

special glasses, pots made of special materials are required, since these glasses, when molten, produce a rapid chemical attack upon ordinary fire-clays. A certain amount of the aluminiferous material of the pot is, in fact, always introduced into the glass by the gradual dissolving action of glass on fire-clay which we have already described. The glass contaminated with these aluminiferous substances differs in density from the rest of the contents of the pot, and therefore ordinarily remains more or less adherent to the walls of the crucible, but the inevitable disturbances which accompany the processes of melting and fining lead to the dissemination of some of this glass through the entire pot in the form of veins or striæ, which are only removed during the stirring process. On the other hand, more of this aluminiferous glass is constantly being formed so long as the glass remains molten, and if disturbances are not sufficiently avoided during the later stages of the process fresh veins may easily be formed.

The actual operations of producing a melting of optical glass begin by the gradual heating-up of the pot in the kiln just described. When the pot has reached a full-red heat or, if fired to a higher temperature in a modern kiln, has been allowed to cool down again to a red heat, the doors of the kiln are opened and the pot drawn out by means of a long heavy iron fork running on wheels; this implement is run into the mouth of the kiln and the tines of the fork are pushed under the pot, and the latter is then readily lifted up and withdrawn from the kiln. Meanwhile the temperature of the furnace has been regulated in such a manner as to be approximately equal to that attained by the heating kiln, so that the pot, when transferred as rapidly as possible from the kiln to the furnace, is not subjected to any very sudden heating; were it attempted to place the new pot in a furnace at full melting heat the entire vessel would fall to pieces. Even under the best conditions it is not possible to avoid the occasional failure of a pot by cracking either at this or a slightly later stage of the process. The latter occurrence is apt to be particularly disastrous, as the pot may then be full of molten glass, which runs out and is lost.

As soon as the empty pot has been put into place, the melting furnace is carefully sealed up by means of temporary work built of large fire-bricks, the whole being so arranged that the mouth of the hood of the pot is left accesssible by means of an aperture in the temporary furnace wall. This aperture can be closed by one or more slabs of fire-clay, and when these are removed an opening is left by which the raw materials are introduced, and through which the other manipulations are carried out.

When this stage of the process is reached, the wagons containing the mixed raw materials are usually wheeled into place in front of the furnace, but the introduction of the materials themselves into the pot is not begun until several hours later, when the furnace has been vigorously heated and an approach to the melting heat has been attained.

When the furnace and pot have attained the necessary temperature, but before the raw materials are introduced, a small quantity of the cullet, which has been reserved for this purpose, is thrown into the pot and allowed time to melt, and then only is the first charge of mixture put into the pot. The object of this proceeding is to coat the bottom and part of the walls of the pot with a layer of molten glass which serves to protect it from the chemical and physical attack of the raw materials during the violent action which takes place when they are first exposed to the furnace heat.

The gradual filling of the pot with molten glass is now carried out by the introduction of successive charges of raw material; as the mixture not only occupies more space than the glass it forms, but also froths up a good deal during melting, the quantities introduced each time must be carefully adjusted so as to avoid an overflow of half-melted glass through the mouth of the pot. As the pot is more and more nearly filled, the space left for the raw materials is proportionately diminished, and the later charges are therefore much smaller than the first few.

When, finally, sufficient material has been introduced to fill the pot completely, the next stage of the process commences. When

the last charge of raw materials has melted, the glass in the pot is left in the state of a more or less viscous liquid full of bubbles of all sizes; it is essential that these bubbles should escape and leave the glass pure and "fine," and this result can only be achieved by raising the temperature of the furnace and allowing the glass to become more fluid, while the rise of temperature also causes the bubbles to expand owing to the expansion of the gas contained in them. In both ways rise of temperature facilitates the escape of the bubbles, and the furnace is therefore heated to the full, and this extreme heat is maintained until the glass is free from bubbles. In the case of the more fusible glasses the temperature required for this purpose is not excessively high, and, indeed, in the case of these glasses care is taken to avoid too high a temperature, as it entails other disadvantages. In the case of the harder crown glasses, however, the difficulty lies in producing an adequately high temperature without at the same time endangering the life of furnace and crucible. The difficulty of freeing the molten glass from bubbles constitutes one of the causes that limit the range of our optical glasses in one direction—still harder glasses could be melted, but it would not be feasible to maintain a temperature high enough to render them fluid enough to "fine."

In the case of other kinds of glass, again, it becomes impossible entirely to remove the bubbles from the molten mass even when very hot and very fluid. The exact cause is not known, but in some kinds of glass the bubbles formed are so minute that even when the glass is perfectly mobile the bubbles show no tendency to escape, while in other kinds of glass there appears to be a steady evolution of minute bubbles as soon as the temperature is raised with a view to removing those already in the glass. As this property attaches to some of the most valuable of the newer varieties of optical glass, opticians and the public have learnt to put up with the presence of minute bubbles in certain lenses and prisms. These bubbles are, however, very minute and do not interfere with the optical performance of the lenses, etc., except to the extent of

arresting and scattering the very small proportion of light that falls upon them; their presence is therefore to be regarded as a small but unavoidable drawback to the use of glasses which offer advantages which completely out-weigh this defect.

Returning to the melting process, we find that the extreme heating required for the purpose of "fining" the glass is continued for a considerable period of time, as long as thirty hours in some cases, the glass being examined from time to time to test its condition as regards freedom from bubbles. This is done by taking a small sample of glass out of the pot and examining it to see if it still contains bubbles. In some works this test is made by taking up a very small gathering of glass on the end of a small pipe and blowing it into a spherical flask; on looking at such a flask in a suitable light the presence of even minute bubbles is readily detected. In other works a simpler process is adopted, a small quantity of glass being ladled out of the pot on the surface of a flat iron rod. It is allowed to cool on the rod, and when pushed off forms a small bar of glass some eight or ten inches long and about an inch wide; in this also the presence of bubbles is easily detected. These test pieces are known among glass-makers as "proofs."

When proofs, taken as just described, have shown that the glass is free from bubbles, the extreme heat of the furnace is allowed to abate, and the fire-clay slabs in front of the mouth of the pot are removed. The next step is that of skimming the surface of the glass. Since most of the materials liable to contaminate the contents of a pot are specifically lighter than the molten glass, they will be found floating on the surface, and the surface glass is therefore removed with a view to ridding the glass of anything that may have been accidentally introduced and that has not melted and become incorporated with the molten mass. This skimming operation is much facilitated if the pot has been filled to such an extent that there is a slight tendency for the glass to overflow at the lip of the pot. If the pot is not quite full, skimming becomes a very difficult operation.

The next steps in the process are those of stirring the molten glass with a view to rendering it homogeneous and free from striæ. The stirrer used for this purpose is usually a cylinder of fire-clay, previously burnt and heated. This is provided with a deep square hole in one end, and it is held at first by means of a small iron bar passed into this hole. By this means the red-hot cylinder of fire-clay is introduced into the open mouth of the pot, and when it has attained approximately the temperature of the molten glass it is dipped into the glass itself, in which it ultimately floats. The operation of dipping the stirrer into the glass is carefully carried out in such a manner as to carry as little air as possible down into the glass; at best, however, the pores of the clay stirrer are full of air, and this must be permitted to escape before stirring is begun, as otherwise minute air bells would be dispersed throughout the glass during the stirring operation. For this purpose the stirrer is left immersed in the glass for several hours while the pot is again closed up and the temperature raised.

When stirring is to begin, the square, down-turned end of a long iron bar is introduced into the corresponding square hole in the upper end of the stirrer, and by this means the fire-clay cylinder is held in a vertical position in the glass and given the steady rotatory movement which constitutes the stirring process. For this purpose the long iron bar just mentioned is made to pass over a swivel-wheel, while a workman moves it steadily by the aid of a large wooden handle. The relative arrangement of the pot, the fire-clay stirrer immersed in the glass, and the bar or "crochet" by means of which it is moved, are shown in plan and vertical section in the sketches of Figs. 17 and 18.

It was for a long time considered essential that the stirring operation should be conducted by hand by specially skilled men who were supposed to know by the "feel" of the glass whether they were moving the stirrer at the right rate for the condition of the glass at any given moment. The whole operation, however, is extremely trying, as the workman is exposed to the heat and glare from the

furnace—particularly as he has to watch the motion of the stirrer in the glass. In modern practice the movement of the stirring bar is actuated by electrically-driven mechanism, and although it is still held that the results obtained are not as good as those achieved by the most skilful hand-stirring, there are very considerable advantages in the regularity and certainty of operation of the mechanical appliances. There can be no doubt, however, that the stirring process as at present conducted is a very imperfect and make-shift operation and that here, perhaps, more than at any other point in the process, there is room for improvement based on careful scientific research.

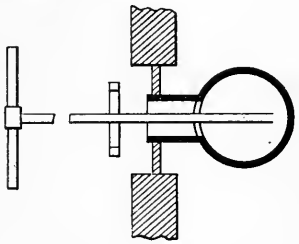

FIG. 17.

With the primitive type of stirrer still used in practice the actual amount of stirring required is very considerable; a certain number of hours' stirring is usually given, but there is no real certainty that this is adequate in any given case. The amount given varies according to the nature of the glass and the size of the pot. For some meltings only four hours are allotted, while for others as much as twenty hours are given.

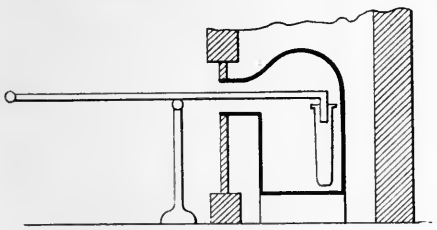

FIG. 18.

During the earlier stages of the stirring process the glass is very hot and mobile, but the stirring is continued, with short intervals devoted to re-heating the glass, until the glass is so cold and stiff that the stirrer can scarcely be moved in it at all.

When the glass has stiffened to such an extent that it is no longer possible to continue the stirring, preparations are made for the final cooling-down of the pot of glass. The fire-clay stirrer is sometimes withdrawn from the glass, but this is laborious, and entails

dragging a considerable quantity of glass out of the pot with the clay cylinder; more usually, therefore, the stirrer is simply left embedded in the glass.

The next object to be accomplished is that of cooling the glass as rapidly as safety will permit until it has become definitely "set"—the purpose being to prevent the recrudescence of striæ as a result of convection currents or other causes which might disturb the homogeneity of the glass. This rapid cooling is obtained in various ways; in one mode of procedure the furnace is so arranged that by opening a number of apertures provided for the purpose cold air is drawn in and the pot and its contents chilled thereby without being moved. This method has the advantage that the pot containing the viscous glass is never moved or disturbed in any way, but on the other hand the cooling which can be effected within the furnace itself is never very rapid, and the furnace as well as the pot is chilled, a proceeding which tends towards rapid deterioration of the furnace. Further, when the glass has been chilled down to a certain point this rapid rate of cooling must be arrested, as otherwise the whole contents of the pot would crack and splinter into minute fragments. Where the pot has been left in the furnace this can only be done by sealing up the whole furnace with temporary brickwork and lutings of fire-clay, leaving it to act as an annealing kiln until the glass has cooled down approximately to the ordinary temperature, a process which occupies a period of from one to two weeks according to the size of the melting. Such enforced idleness of a melting furnace is of course very undesirable from an economical point of view, and it is generally avoided by adopting the alternative method of drawing the pot bodily out of the furnace as soon as the stirring operation is ended. For this purpose the temporary brickwork forming the front of the furnace is broken down, and with the aid of a long crowbar the bottom of the pot is levered up from the bed or siege of the furnace to which it adheres strongly, being bound down by the sticky viscous mass of molten glass and half-molten fire-clay which always accumulates on the bed of the furnace. The pot being temporarily

held up by the insertion of a piece of fire-brick, the tines of a long and heavy iron fork running on a massive iron truck are introduced beneath the pot; an iron band provided with long handles is then passed around the pot, and the latter is then drawn forward by the aid of suitable pulley blocks. The tines of the fork are then raised, and the pot is wheeled out of the furnace and deposited upon a suitable support. Here it is allowed to cool to the requisite extent, when it is again picked up on the tines of the fork and deposited in an annealing kiln which has been previously warmed to a suitable temperature. In the case of certain glasses, which have a strong tendency to devitrify during cooling, the degree of chilling which results from mere exposure to cold air outside the furnace is not sufficient and more rapid cooling is induced, either by a powerful air-blast from a fan or even by jets of cold water playing on the pot. It will be seen that this handling of a heavy mass of intensely hot material involves much labour, while there is also a risk of losing the glass if the pot should break before the glass has set sufficiently. Every care is taken to prevent such an accident, the pot being wrapped round with chains or otherwise supported in such a way that a small crack could not readily develop into a large gap.

When such a melting of glass has cooled sufficiently, either in the furnace or in the annealing kiln, to be safely handled, the whole pot is drawn out, and the fire-clay shell, which is generally found cracked into many pieces, is broken away by the aid of a hammer. Under favourable circumstances the whole of the glass may have cooled intact as one solid lump sometimes weighing over half a ton. Unless special care is taken, however, it is usual to find the glass more or less fissured, a number of large lumps being accompanied by a great mass of small fragments. These are now picked over, and all those which are free from visible imperfections or which can be readily detached from such imperfections by the aid of a chipping hammer are put upon one side for further treatment.

The next step of this treatment consists in moulding the rough broken lumps into the shape of plates, blocks, or discs according to the purpose for which the glass may be required by the optician. The plant used for the moulding process varies widely, but in all cases the operation consists in gradually heating the glass in a suitable kiln until it is soft enough to adapt itself to the shape of the mould provided for the purpose. In some cases these moulds are made of fire-clay, and the glass is simply allowed to settle into them by its own weight; in other cases iron moulds are used, and the glass is worked into them by the aid of gentle pressure from wood or metal moulding tools. In yet other cases, particularly where the glass is required in the form of small thin discs or where it is to be formed into the approximate shape of concave or convex lenses, the aid of a press is sometimes invoked.

In all cases the moulding process is followed by the final annealing, which consists in cooling the glass very gradually from the red heat at which it has been moulded, down to the ordinary temperature. The length of time occupied by such cooling depends very much upon the size of the object and also upon the degree of refinement to which it is necessary to carry the removal of small internal strains in the glass. For many purposes it is sufficient to allow it to cool down naturally in a large kiln in the course of six or eight days. For special purposes, however, where perfect freedom from double refraction is demanded, much greater refinements are required, and special annealing kilns, whose temperature can be accurately regulated and maintained, are employed. In these the annealing operation can be carried out so gradually that a rate of cooling in which a fall of 1° C. occupies several hours can be maintained, so that very perfectly annealed glass can be produced even in discs or blocks of large size.

When removed from the annealing kiln the plates or discs of optical glass are taken to a grinding or polishing workshop, where certain of their faces or edges are ground and polished in such a way as to permit of the examination of the glass for bubbles, striæ and other

defects in the manner indicated in the previous chapter. As the amount of sorting that can be done while the glass is still in rough fragments is necessarily very limited, it follows that a considerable proportion of the glass which has been moulded and annealed must be rejected as useless when thus finally examined. A yield of perfect optical glass, amounting to 10 or at most 20 per cent. of the total contents of each pot, is therefore all that can be expected, and smaller yields are by no means infrequent—a consideration that will serve to explain the relatively high price of optical as compared with other varieties of glass.

A consideration of the various factors that are involved in the production of a piece of perfect optical glass will make it apparent that the cost and difficulty of its production increases rapidly with the weight of the piece to be produced, so that it is not surprising to find that the price of very large discs of perfect optical glass such as those required for large astronomical telescopes, reaches figures which become prohibitive when very large sizes are considered. Thus, while it is quite possible to obtain say 100 pounds of good glass from a single melting if the glass is to be used in the form of pieces not weighing more than five or six pounds each, it is only rarely that a single block of perfect glass can be found weighing 100 pounds. In the former case the best pieces can be picked, the worst defects can be eliminated by chipping the rough fragments, and at a later stage other defective pieces can be cut off or ground away ; not so where a large single block is required. A single fine vein, perhaps too small to be visible to the unaided eye, may be found to run through a whole block in such a way that it cannot be removed without breaking or cutting up the whole piece, and it will be seen that the frequency with which this is liable to occur increases with the volume of the piece required. The difficulties of re-heating and moulding are also increased enormously with the size of the individual pieces of glass that have to be dealt with, and where very large pieces have to be heated and cooled accidental breakage becomes a serious risk. In view of these difficulties it is not sur-

prising to find that the dimensions of our astronomical refractors appear to have approached their limit, but rather are we led to admiration of the skill and enterprise that has pushed this limit so far as to produce discs of optical glass measuring as much as one metre in diameter.

CHAPTER XV

MISCELLANEOUS PRODUCTS

THE field of glass manufacture is so wide and the number and variety of its products so great, that in the limited compass of this volume it is impossible fully to enumerate them all; there are, however, a certain number of these products which, while of considerable importance in themselves, yet do not fall readily under any of the headings of the preceding chapters. A short space will therefore be devoted to some of these in this place.

Glass Tubing.—A widely-useful form of glass is that of tubes of all sizes and shapes, ranging from the fine capillary tubes used in the construction of thermometers to the heavy drawn or pressed pipes that have been employed for drainage and other purposes. The process of manufacture employed varies according to the size and nature of the tube that is required. Thus lamp-chimneys are really a variety of tube, used in short lengths and made of relatively wide diameter and thin walls. These are not, however, ordinarily made in the form of long tubes cut into short sections, but—as has already been mentioned—they are blown into moulds in the form of a thin-walled cylindrical bottle, whose neck and bottom are subsequently removed. By this process the various forms of chimneys for oil lamps, having contractions at certain parts of their length, can be readily produced. They are frequently blown in pairs.

The articles more strictly described as glass tubes are, however, produced by a process in which actual blowing plays only a very minor part. A gathering of suitable size is taken up on a pipe, a very small interior hollow space is produced by blowing into the pipe, and then the gathering is elongated by swinging the pipe in a suitable

manner. The end of the elongated gathering furthest from the pipe is then attached to a rod or " pontil " held by a second workman, and the two men then proceed to move apart, drawing out the gathering of glass between them. According to the bore and thickness of wall required in the tube, the men regulate the speed at which they move apart ; the thinner the tube is to be the more rapidly they move, in order to draw the glass out to a sufficient extent before it hardens too much. The rate of drawing must, of course, also be adapted to the nature of the glass in question, and this will vary very widely. For the production of the smaller bored tubes the men find it necessary to separate at a smart trot, while heavy tubes such as are used for gauge-glasses, are drawn of hard glass by a very gradual movement. In some cases, the setting of the glass, when the tube has attained the desired thickness, is hastened by the aid of an air-blast, or—in more primitive fashion—by boys waving fans over the hot glass. In any case, suitable troughs are provided for receiving the tube when drawn, and from these the tube is taken to an annealing kiln to undergo this necessary operation.

The glass used for the production of tubing varies very widely according to the purpose for which the product is intended. Almost any of the more usual varieties of glass can be readily drawn out into tubes, and the choice of the kind of glass to be employed is therefore based on other considerations. Tubing required for the use of the lamp-worker, *i.e.*, for the production of instruments or other articles by the aid of the glass-blower's blow-pipe, must have the capacity of undergoing repeated cooling and heating without showing signs of crystallisation (devitrification), while reasonable softness in the flame is also required. For this purpose, also, glass containing lead is not admissible, since this is liable to blacken under the influence of the blow-pipe flame. Soda-lime glasses rather rich in alkali are most frequently used for these purposes ; one consequence of their chemical composition, however, is that such glass tends to undergo decomposition when stored for any length of time, more especially in damp places. Frequently this decomposition only manifests itself

on heating the glass in a flame, when it either flies to pieces or turns dull and rough on the surface. Such glass is sometimes said to have "devitrified," but this is not really the case; what has actually happened is that atmospheric moisture has penetrated for some little distance into the thickness of the glass, probably hydrating some of the silica; on heating, this moisture is driven off, with the result that either a few large cracks or innumerable fine ones, are formed. In the latter case these do not readily disappear when the glass is softened and a dull, rough surface is left at the end of the operation.

For purposes where the glass is to be exposed to high temperatures, tubing made of so-called "hard glass" is employed. This is practically a form of Bohemian crystal glass, the chemical composition being that of a potash-lime glass rather rich in lime. To some extent this Bohemian hard glass has been superseded by the special "combustion tube" glass introduced by Schott, of Jena, but now made by several British firms. This is a very refractory borosilicate glass containing some magnesia; it certainly withstands higher temperatures than hard Bohemian glass, and is rather less sensitive to changes of temperature; on the other hand, it has the inconvenient property of showing a white opalescence when it has once been heated, and this, after a time, renders the glass completely opaque.

For many purposes, where heat-resisting qualities are chiefly required, ordinary glass finds a formidable rival in the shape of vitrified silica, which has long been available as a satisfactory commercial product. This substance offers the great advantage that for most ordinary purposes it may be regarded as entirely infusible, since the intense heat of an oxygen-fed flame is required to soften or melt the silica. Further, vitreous silica has an extremely low coefficient of expansion, and appears also to have a rather high coefficient of thermal conductivity. The result is that tubes and other articles made of this material possess an astonishing amount of thermal endurance (see Chapter II.).

A white-hot tube or rod of this material can be plunged into cold water with impunity, and no special care need be exercised in

heating or cooling objects made of this substance, unless articles of great size and thickness are involved, and even with these only little caution is needed. The only disadvantages which must be balanced against the great advantages just named lie in the relatively high cost of the articles and in their somewhat sensitive behaviour to certain chemical influences. As regards cost, vitreous silica is at present available in two different forms; in the first form it resembles ordinary glass very closely in appearance, the shape and finish of the tubes and vessels of this kind being almost equal to that of good glass ware. This silica glass has, in fact, been worked from molten silica in a way more or less analogous to that in which ordinary glass is worked, the great extra cost of the silica ware being due, in part, at all events, to the extremely high temperature required for melting and working this material; ordinarily, in the production of the class of silica ware now referred to, this heat is generated by the liberal—and therefore expensive—use of oxygen gas. In great contrast to this glass-like, transparent silica ware is the other form in which this material is available. This is a series of products obtained from the fusion of silica in special forms of electric furnace; in this ware the minute bubbles so readily formed in the fusion of all forms of quartz are not even partially eliminated, and by their presence—often in the form of long-drawn-out, capillary hollows—they impart to this ware its very characteristic milky appearance. The price of this product, which is mostly used in the form of tubes, although such articles as basins, crucibles, and even muffles and other apparatus of considerable size are available, is much lower than that of the transparent variety, being in fact decidedly lower than that of the best porcelain; on the other hand, even this price is considerably above that of the best glass tubing.

Apart from the question of cost, the use of silica ware is further limited by its sensitiveness to all forms of basic materials. Thus alkaline solutions cannot be allowed to come into contact with this substance, since they attack it vigorously, especially when warm. At high temperatures all basic materials produce a rapid attack on

silica ware, the silica, in fact, behaving as a strongly acid body at and above a red heat. The attack which occurs when such a substance as iron or copper oxide is allowed to come into contact with heated vitrified silica is so rapid that a tube is completely destroyed in a few minutes, the formation of silicates resulting in the cracking and disintegration of the whole piece. While, therefore, silica ware, especially in its cheaper forms, undoubtedly possesses great advantages and possibilities, its use must be carried on with careful reference to its chemical nature.

Vitreous silica, in addition to the uses and advantages just named, has also an interest from the optical point of view ; this arises from the fact that it is transparent to short (ultra-violet) light waves to which all ordinary varieties of glass are completely opaque. Although special glasses have been produced which are more transparent to ultra-violet rays than ordinary glass, even these fall far short of silica in this respect. This property of transparence to ultra-violet light is utilised in two widely different directions. One of these is in the production of ultra-violet light when required for medical or other special purposes ; a most energetic source of such rays is available by the use of tubes of vitrified silica within which the mercury-vapour arc is produced. In another direction the employment of quartz lenses makes it possible to take advantage of the optical properties of ultra-violet light in connection with microscopy ; for the purpose of constructing a perfect optical system, crystalline quartz would be useless, since its property of double refraction is apt to interfere with the performance of the lenses. This is now overcome by the use of vitreous silica lenses, in the case of the "ultra-violet microscope." So far, however, it has only been possible to produce quite small pieces of vitreous silica sufficiently free from bubbles to be used for optical purposes. The great difficulty lies not so much in merely melting the quartz down as in freeing it from the air bubbles enclosed within it ; the course usually adopted with glass, of raising the temperature and allowing the bubbles to rise to the surface becomes impossible in this case, because the silica itself

begins to vaporise and even to boil vigorously at temperatures not very far above its melting point. Two American workers have claimed to be able to overcome this difficulty by the use of both vacuum and high pressure applied at the earlier and later stages of the fusion process respectively, but vitreous silica in large and perfectly clear blocks is not yet available.

We have already indicated that glass tubing and rod form the basis upon which the glass-worker, with the aid of the blow-pipe or "lamp," fashions his productions, which, of course, include a great number of scientific instruments and appliances used more especially in the field of chemistry. In another direction also glass tubing serves as a basis for a branch of the glass industry; this is the manufacture of certain classes of glass beads, which are formed by cutting up a heated glass tube of suitable diameter and colour into short, more or less spherical sections. In some cases the colour of the beads is secured by using glass of the desired tint, but in other cases the beads are made of colourless glass, and a colouring substance is placed in the interior of the bead.

Solid glass rods are also employed for a variety of purposes; their mode of manufacture is exactly analogous to that of tubing, except that the gathering is drawn out without having first had a hollow space produced at its centre by the blower. In its most attenuated form glass rod becomes glass thread or fibre; this is produced by drawing hot glass very rapidly, the resulting thread being wound on a large wheel. At one time this material found considerable use, since it was found possible to spin and weave the thinnest glass fibres into fabrics which could be used for dress purposes. It is not, however, to be regretted that this fashion has neither extended nor survived, since it was certainly liable to produce serious injury to health. It is a well-known fact that there are few more injurious or even dangerous substances to be inhaled into the human throat and lungs than finely-divided glass; glass fibre, moreover, when subjected to constant bending and wear, is bound to undergo frequent fracture, and the atmosphere of a ball-room, for example, in which

several such dresses were worn would soon be contaminated with innumerable fine, sharp particles of glass which would produce an injurious effect on those inhaling them. At the present time glass fibre is used for little else than the "glass wool" required for certain special purposes in chemical laboratories.

Fused quartz or silica fibres, of extreme tenuity, but of relatively very great strength, are employed in many scientific instruments, where their extreme lightness and perfect elasticity and freedom from what is known as "elastic fatigue" renders them of very great value. These fibres are not drawn from a mass of molten silica, as is done with glass, but are produced by attaching a nail or bolt to a small bead of fused silica produced by the aid of an oxygen-fed blow-pipe; the nail or bolt is then suddenly shot away down a long passage or similar space by means of a cross-bow, drawing a very fine fibre of silica with it; the most difficult part of this operation, however, consists in finding and handling the fibres thus produced.

Artificial Gems.—The fact that pieces of suitably-coloured glass can be made to show a superficial, but sometimes more or less deceptive, resemblance to precious stones, has led to the manufacture of imitation jewels of all descriptions. The glass used for this purpose is usually a very dense flint glass whose high refractive index facilitates the imitation which is aimed at. The external shapes of gems are, of course, readily imitated by cutting and grinding the glass, while the requisite colours are attainable by means of the colouring materials described in Chapter XII. To a casual observer the difference in sparkle and brilliance which arises from the difference between the refractive index of the heavy flint glass (about 1·8) and that of minerals (which ranges from 1·7 to 2·2) is not readily apparent, but closer examination will at once reveal the difference. The determination of the optical constants by means of a refractometer would at once reveal the true character of the imitation, but an even readier test is that of hardness. The dense flint-glass is naturally soft, and is readily scratched by most of the harder minerals while the precious stones, more particularly garnets, rubies and

diamonds, are very hard. If an attempt is made to scratch an ordinary sheet of window-glass, it will be found that most real precious stones will do so readily, while flint glass imitations will fail to make more than a slight mark, which is more smear than scratch. The test by determining the specific gravity is also obviously applicable, since the flint glass will readily betray its presence by its high density (over 4).

In quite a different class from the imitation gems made of cut flint glass are the artificial gems, which in nature and composition are exact reproduction of natural gems, but which have been produced by artificial processes. As far as the writer is aware these are only found in any large numbers in the case of the ruby, but in that case, at all events, it is said that the production of the artificial crystals is at least as costly as the purchase of the natural stones. There can, however, be very little doubt that as the processes of fusion and crystallisation become better known and understood, and the chemistry of silicate minerals is developed, the artificial production of mineral crystals in, at all events, moderate sizes will become increasingly possible; it is even to be hoped that their production will be so far perfected as to place their really valuable properties at the service of man.

Chilled Glass.—In all the processes of glass manufacture described in the present book, annealing has always played an important part. The glass, after it has undergone its last treatment under the influence of heat, is subjected to a gradual cooling process with the object of freeing it from the internal strains which it would otherwise retain, and which would, ordinarily, endanger its existence and interfere with its use. It is, however, well known that objects of glass subjected to such internal strains as result in a compressive stress on the glass near the surface, are less liable to injury, and are apparently stronger than when the glass is annealed and the stresses are removed. On the other hand, glass surfaces under tension are extremely delicate and fragile. In some respects, therefore, glass which has not been annealed may appear to be stronger than the

annealed product. The well-known case of the Rupert's drop is an example of this kind. Rupert's drops are produced by dropping molten glass into water; they generally take the form of a more or less spherical body having a long tail, tapering off into a thread, attached to it. Such a Rupert's drop may be struck with a heavy hammer, and will safely resist a blow that would splinter a similar body made of annealed glass. If, however, the surface be scratched, or the tip of the tail be broken off, the entire "drop" breaks up, sometimes with a violent explosion, into minute fragments. Numerous inventors, among whom De la Bastie and Siemens figure most conspicuously, have endeavoured to utilise these properties of chilled glass, not exactly by seeking to produce that extreme degree of internal strain which is characteristic of the Rupert's drop, but by producing what they describe as "tempered" glass, in which the internal strains have been reduced by less violent cooling to such an extent as to retain some of the advantages of the hardened, internally strained condition while approximating more or less to the safer state of annealed glass. At one time articles of this kind were frequently seen as curiosities, such as tumblers that could be dropped on the floor without breaking, etc., but those articles generally ended by receiving a slight scratch or chip and promptly falling into fragments. As a matter of fact, however, some tempered glass is actually manufactured by the firm of Siemens at the present time for special purposes. De la Bastie's process was tried in England, and some success was claimed for it; but it is not in commercial operation at the present time, and never appears to have attained any great importance.

Massive Glass.—Enthusiasts for the extension of the use of glass have endeavoured to apply it to a great variety of purposes, including the construction of buildings and the paving of streets. In the former case, which was exemplified at the Paris Exhibition of 1900, advantage was taken of the light-transmitting power of the material, but although the buildings erected with large blocks of cast glass were not displeasing in effect, this use has not found any considerable

extension. For paving purposes, the hardness and durability of glass are the only useful qualities, and here also—although several trials have been made in France—no signs of any considerable application of the new products are as yet visible. What has been said above with reference to the injurious character of glass dust applies, further, to glass pavements, since their natural wear would result in the formation of considerable quantities of this dust. The advocates of glass paving, however, suggest that the hardness of glass would greatly reduce the actual amount of wear, and that consequently the dust would be reduced considerably. This is a matter which prolonged experience alone can decide, but it does not seem obvious that glass blocks should wear more slowly than stone setts made of good granite, for example. On the other hand, the glass blocks could probably be produced more cheaply, since the labour of cutting to size would be obviated by casting the blocks to the desired dimensions.

Water-glass, or silicate of soda or potash, is perhaps scarcely to be classed under the heading of "Glass Manufacture" at all, but it bears a certain relationship to glass in several ways. Thus one of the modes of manufacturing water-glass is by the fusion of sand and alkali in tank-furnaces somewhat resembling those used for glass production; the fused silicate, moreover, solidifies as a vitreous mass, in which respect it also resembles such substances as borax, etc. The uses of silicate of soda and potash are, however, so far removed from the field of glass-manufacture that we cannot enter into them here.

In concluding this chapter, we wish to describe one more product of the glassworks, and this includes some of the most impressive and splendid examples of the glass-maker's art. These are the great mirrors and lenses by whose aid our lighthouses and searchlights send forth their powerful beams of light. Although these objects are called "mirrors" and "lenses," since they fulfil the functions of such optical organs, yet in their nature and mode of manufacture they are so far removed from the glass used for the production of

other kinds of lenses that they could not be included under the heading of "optical glass."

The characteristic feature in the manufacture of optical glass is the manner in which each separate pot or melting is allowed to cool down and to break up into irregular fragments which are subsequently moulded to the desired shape. Were it attempted to manufacture the large glass bodies required for lighthouse purposes in this manner, the cost would approximate to that of the large discs used for telescope objectives, and this would of course be entirely prohibitive. The requirements as regards colour, homogeneity and freedom from other defects, which must be met in lighthouse lenses, are further not nearly so stringent as those which are essential in ordinary optical work of good quality. The reason for this difference arises from the fact that lighthouse lenses and searchlight mirrors are used merely to impart a desired direction to a beam of light, and not for the purpose of producing sharply-defined images; slight irregularities in the glass are therefore not of such serious importance.

Lighthouse glass can therefore be produced by rather less elaborate means; although every care is taken to make the glass as perfect as possible, it is brought into approximately the desired form by casting the molten glass in iron moulds of the proper shape. When removed from these moulds and annealed, the glass is fixed on large revolving tables and ground and polished to the final shape of lenses and annular lens-segments as required for the various types of Fresnel lighthouse lenses. In this way complete rings, forming annular lenses, are produced up to 48 inches diameter. Rings of larger size are usually built up of a number of segments, and these built-up rings sometimes have a radius as large as 7 feet. For the majority of lighthouse lenses, it should be added, a hard soda-lime glass having a refractive index of 1·50 to 1·52 is used, but for special purposes a dense flint glass having a refractive index of 1·63 is employed.

Mirrors for searchlight purposes are of very varied forms and sizes, the shape depending largely upon the particular form of beam which they are designed to project. For many purposes a parabolic form

is required, while in others, where a flat, fan-shaped beam is to be produced, a form having an elliptical section in a horizontal plane, and a parabolic section in the vertical plane is required. In most cases these mirrors are produced by bending plates of glass, previously raised to the necessary degree of heat, over suitably shaped moulds, the surface being subsequently re-polished to remove any roughness resulting from the bending process. Another type of mirrors is that known as "Mangin," which has two spherical surfaces placed eccentrically in such a way that the centre of the mirror is considerably thinner than the periphery; in this type of mirror the reflecting action of the back surface is modified by the refracting action of the front surface, but both are spherical, and can therefore be accurately ground and polished by the usual mechanical means. Such mirrors are manufactured of single pieces of glass up to 6 feet in diameter.

APPENDIX I

THE COMPOSITION OF SOME TYPICAL GLASSES (CHEMICAL ANALYSES)

ALTHOUGH the general type of composition of each of the more important varieties of glass has been indicated in the text of the various chapters, a table of the chemical composition of some typical examples as found by careful and expert chemical analysis is here added. It should be noted, however, that the chemical analysis of glass is a matter of great difficulty, requiring much skill and experience, particularly in the case of complex glasses which may contain boron and fluorine. Many published analyses must, for this reason, be regarded with caution. It should further be borne in mind that a "batch" cannot be laid down, by simple calculation from an analysis, to produce a glass of the same chemical composition; discrepancies, which may be considerable, arise from losses by volatilisation, and the composition of the glass is also affected by solution of material derived from the pot or other containing vessel. The composition of a "batch" which shall produce a glass of given analysis can thus, as a rule, be arrived at only after some experiments, although experience of similar cases may serve as a guide to some extent.

ANALYSES OF GLASSES.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
Silica (SiO_2)	73·88	74·28	54·92	76·78	72·86	66·58	66·44	53·18	64·60	76·02
Alumina (Al_2O_3)	2·24	3·24	1·28	0·72	6·24	3·84	1·76	0·50	6·24	0·64
Ferric Oxide (Fe_2O_3)	tr.	tr.	tr.	tr.	tr.	—	0·24	tr.	tr.	tr
Manganese Oxide (MnO)	tr.	tr.	tr.	tr.	tr.	0·28	tr.	tr	tr.	tr.
Lime (CaO)	tr.	tr.	tr.	6·52	0·35	7·18	12·90	0·14	tr.	7·38
Magnesia (MgO)	tr.	tr.	0·20	0·24	0·20	0·17	0·52	0·32	0·32	0·30
Lead Oxide (PbO)	—	—	34·93	—	—	—	6·45	33·74	—	—
Boric Anhydride (B_2O_3)	16·48	15·02	—	—	10'43	0·91	—	—	8·70	—
Arsenious Oxide (As_2O_3)	0·73	0·73	0·99	—	—	—	—	—	—	—
Antimony Oxide (Sb_2O_3)	—	—	—	—	—	—	—	—	—	—
Zinc Oxide (ZnO)	—	—	0·82	—	—	6·24	—	—	10·43	—
Sulphuric Anhydride (SO_3)	—	—	—	—	—	—	—	—	—	—
Potash (K_2O)	tr.	tr.	4·54	4·74	0·10	tr.	1·55	11·48	tr.	7·70
Soda (Na_2O)	6·67	6·73	2·08	11·14	9·82	14·80	9·82	0·42	9·71	7·60
Fluorine (F)	—	—	—	—	—	—	—	—	—	—
TOTAL	100·00	100·00	99·76	100·14	100·00	100·00	99·68	99·78	100·00	99·64

1. Incandescent gas chimney. (Jena.)
2. Miner's lamp glass. (German make.)
3. „ „ „ (French make.)
4. Austrian make lamp glass.
5. Thermometer glass, Jena 59^{111}.
6. Thermometer glass, Jena 16^{111}.
7. „ „ Verre dur Baudin. (French.)
8. „ „ (English.)
9. Glass Beaker, new Jena glass.
10. „ „ Bohemian. (Kavalier.)

Analyses Nos. 1 to 9 inclusive, by W. H. Withey, B.A., of the National Physical Laboratory.

Analysis No. 10, by Walker, *Journ. Amer. Chem. Soc.*, XXVII., 865, 1905.

ANALYSES OF GLASSES—*continued.*

	11.	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
Silica (SiO_2)	63·40	71·56	69·40	72·48	71·64	75·27	67·71	70·80	71·82	72·29	64·96
Alumina (Al_2O_3)	10·92	0·44	0·90	1·04	0·73	1·91	1·94	1·33	2·35	2·55	5·86
Ferric Oxide (Fe_2O_3)		0·26		0·18	0·05	—	0·11	0·23	0·15	0·16	0·36
Manganese Oxide (MnO)		0·20		—	—	—	—	—	—	—	—
Lime (CaO)	6·44	15·18	11·04	12·73	11·92	0·63	—	13·55	13·94	13·65	7·59
Magnesia (MgO)	tr.	0·28	0·53	0·21	0·21	0·07	—	0·32	0·30	0·30	0·58
Lead Oxide (PbO)	—	—	—	—	—	—	—	—	—	—	3·04
Boric Anhydride (B_2O_3)	7·30	—	—	—	—	15·18	13·42	—	—	—	—
Arsenious Oxide (As_2O_3)	—	—	—	—	—	—	—	—	—	—	—
Antimony Oxide (Sb_2O_3)	—	—	—	—	—	1·98	6·99	—	—	—	—
Zinc Oxide (ZnO)	—	—	—	—	—	—	0·81	—	—	—	—
Sulphuric Anhydride (SO_3)	—	—	—	—	—	—	—	0·29	0·19	0·16	—
Potash (K_2O)	2·20	tr.	1·34	—	—	—	—	—	—	—	5·17
Soda (Na_2O)	9·34	12·01	16·54	13·36	15·45	4·96	9·02	13·48	11·15	10·89	8·93
Fluorine (F)	—	—	—	—	—	—	—	—	—	—	7·88
											104·37
											3·31 Less O = F.
TOTAL	99·60	99·93	99·75	100·00	100·00	100·00	100·00	100·00	99·90	100·00	101·06

11. Beaker, English make.
12. Plate glass.
13. White glass bottle.
14. White double rolled (figured) plate.
15. German microscope cover glass.
16. Jena heat resisting globe for high pressure gas.
17. Heat resisting chimney. (Monopol.)
18. Rolled plate.
19. „ „
20. Sheet glass.
21. White pot opal glass.

Analyses 11, 12 and 13, by W. H. Withey, B.A., of The National Physical Laboratory.

APPENDIX II

BIBLIOGRAPHY

THE existing literature of glass manufacture is still very limited; in the English language, in particular, there are few books and papers on the subject. Recently, however, matters have been very much improved as a result of the activities of the Society of Glass Technology, whose *Journal* constitutes a most valuable source of information both in original papers and in abstracts from other publications. The French and German literature of the subject is a little more extensive. In giving a list of the works, and more particularly in referring to those which he has consulted in the preparation of the present volume, the author thinks it will be an advantage to indicate their scope, and, to some extent, what he believes to be their value, in order to save the student the trouble of seeking out comparatively inaccessible works only to find that they contain little that is of value for his purpose.

English Books and Papers on Glass Manufacture.

The Principles of Glass Making (George Bell & Sons). By Powell & Chance. An elementary book giving a clear and concise account of the older processes, more especially in connection with flint and plate-glass.

Glass and Glass Manufacture (Pitman & Sons). By P. Marson.

Glass. Articles in 9th Edition of Encyclopædia Britannica. A detailed account of processes, more or less covering the entire subject, but the processes described are mostly obsolete at the present time.

Glass. Article in Supplement to 9th Edition of Encyclopædia Britannica. By Harry J. Powell. A brief summary of more recent developments. Particularly valuable in reference to artistic English flint glass.

Glass. Articles by H. J. Powell and W. Rosenhain in 11th Edition, Encyclopædia Britannica.

Jena Glass. By Hovestadt, translated by J. D. and A. Everett. Contains a full account of the scientific work on glass and its practical application, done in connection with the Jena Works of Schott. Particularly interesting in connection with the subjects of Chapters I., II.,

XIII., and XIV. As the title indicates, the book is written from the Jena point of view, and scarcely does justice to work done elsewhere. The book has gained considerably at the hands of the translators.

Some Properties of Glass. By W. Rosenhain. (Transactions of the Optical Society of London, 1903.) Gives a brief account of the properties of glass as affecting its optical uses.

Possible Directions of Progress in Optical Glass. By W. Rosenhain. (Proceedings of the Optical Convention, London, 1905.) Has been referred to in the text of this book (Chapter XIII.).

Catalogue of the Optical Convention Exhibition, London, 1905. Contains historical and general notices of optical and lighthouse glass, glass-working machinery, etc.

Glass for Optical Instruments. By R. T. Glazebrook. (Cantor Lectures to the Society of Arts.) Gives an account of modern optical glass manufacture.

Optical Glass. By W. Rosenhain. (Cantor Lectures to the Royal Society of Arts.) Deals with the manufacture of optical glass and the problems which arise in connection with efforts to improve the process.

Old English Glasses. By Albert Hartshorne. Gives an account of the history of glass-making in England.

The Methods of Glass Blowing. By W. Shenstone. Describes the manipulation of glass-blowing for experimental purposes, *i.e.*, lamp work.

French Books on Glass Manufacture.

Guide du Verrier. By G. Bontemps. A classical work by one of the greatest experts of his day. Much of the contents of the book is, however, entirely out of date at the present time. The book is interesting as being the work of the man who introduced optical glass manufacture into England.

Verres et Emaux. By L. Coffignal. Chiefly of interest in connection with the subjects of Chapter IX.

Le Verre et le Crystal. By J. Henrivaux. (P. Vicq Dunod et Cie., Paris.) A lengthy book profusely illlustrated and giving a great wealth of detailed information. The writer was for some time the general manager of one of the largest plate-glass manufactories in Europe; his account of plate-glass manufacture is, therefore, especially valuable. Much space in this book is devoted to historical and æsthetical matter.

La Verrerie au XX^{ieme} Siècle. By J. Henrivaux. (Paris, R. Bernard et Cie., 1903.) Practically a supplement to the preceding; some of the processes and products described are, however, not of a practical nature. Chiefly valuable for recent developments in plate-glass and bottle-glass manufacture.

German Books on Glass Manufacture.

Die Glasfabrikation. By R. Gerner. (A. Hartleben's Verlag, Vienna and Leipzig, 1897.) A concise and clear account of most of the more important processes of glass manufacture. Very practical in character. The information given appears to be reliable, although far from complete.

Die Herstellung Grosser Glaskoerper and Die Bearbeitung Grosser Glaskoerper. By C. Wetzel. (Hartleben's Verlag, Vienna and Leipzig, 1900 and 1901 respectively.) Describes numerous special processes and appliances devised for use in connection with large glass objects. Some of these descriptions, however, appear to be little more than transcripts from patent specifications.

Glasfabriken und Hohlglasfabrikation. By R. Dralle. (Leipzig, Baumgaertner, 1886.) Looked upon as a classic in Germany. Gives detailed plans and drawings of entire bottle works, including furnaces and all accessories. Deals principally with bottle manufacture.

Die Glasfabrikation. By Dr. E. Tscheuschner. (Weimar, B. H. Voigt, 1888.) A full detailed account of all processes known at the time. The rapid progress of modern practice has, however, already rendered this book to some extent obsolete.

Jenaer Glas. By Hovestadt. Already referred to in respect of the English translation.

Der Sprechsaal. (Schmidt, Weimar.) A trade journal devoted to the discussion of technical matters relating to the glass and ceramic industries. Occasionally contains articles and abstracts of technical or scientific interest in connection with glass manufacture.

In addition to the books and papers named in the above list, a great number of scientific papers, notes, etc., are to be found scattered throughout the technical and scientific publications of the world; those that have proved of real interest and importance have, however, left their mark on the industry, and will be found described or referred to in connection with the various branches of manufacture described in the present volume or in the books named above.

In addition to the Literature of Glass Manufacture proper, there is now an extensive literature dealing with *Refractories*, much of which has an important bearing on Glass Manufacture. A full bibliography of this subject cannot be given here, but important references to it will be found in :—

The Journal of the Society of Glass Technology (abstracts), which has already been mentioned.

The Journal of the Ceramic Society (Refractories Section); and

The Transactions of the Faraday Society ("General Discussion on Refractories").

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